IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

IJPEIJ et al.

Appln. No. 10/567,098

Filed: February 3, 2006

Confirmation No. 4833

Atty. Ref.: 4662-147

T.C. / Art Unit: 1713

Examiner: C.C. Lu

FOR: PROCESS FOR THE PREPARATION OF A METAL-ORGANIC COMPOUND COMPRISING AT LEAST ONE IMINE LIGAND

* * *

APPEAL BRIEF UNDER 37 CFR § 41.37

June 9, 2009

Mail Stop Appeal Brief – Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Appellants submit this Brief to appeal the Examiner's final rejection as set forth in the Office Action mailed January 9, 2009 (the "final Office Action"). The fee required under 37 CFR § 41.20(b)(2) is submitted herewith.

The Notice of Appeal was filed on April 9, 2009. Thus, submission of this Brief is timely.

Reversal of the Examiner's rejection of claims 1-5 and 11-15 by the Board of Patent Appeals and Interferences (the "Board") is respectfully requested.

I. REAL PARTY IN INTEREST

The assignee, DSM IP ASSETS B.V. holds all rights in the subject invention, as well as the invention disclosed and claimed therein, by assignment from the inventors.

II. RELATED APPEALS AND INTERFERENCES

Appellants, the assignee, and its legal representative do not know of any prior or pending appeal, interference, or judicial proceeding which is related to, directly affects or is directly affected by, or has a bearing on the Board's decision in this appeal.

III. STATUS OF CLAIMS

Claims 1-5 and 11-15 stand rejected. They are at issue in this appeal and listed in the Claims Appendix.

Claims 6-10 and 16 are objected to. They are not at issue in this appeal.

IV. STATUS OF AMENDMENTS

No amendment was filed subsequent to final rejection.

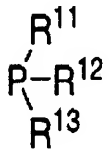
V. SUMMARY OF CLAIMED SUBJECT MATTER

The invention involved in this appeal is directed to a process for the preparation of a metal-organic compound comprising at least one phosphinimine ligand (see pending claim 1). The process comprising contacting a HA adduct of a phosphinimine ligand compound according to formula 1 with a metal-organic reagent of formula 2 in the presence of at least 2 equivalents of a base, wherein HA represents an acid, of which H represents its proton and A its conjugate base,

with **Y=N-H** as formula 1,

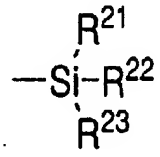
and $\mathbf{M^{v}(L_1)_k(L_2)_l(L_3)_m(L_4)_nX}$ as formula 2,

and wherein Y is defined by the formula :



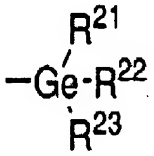
(formula 3)

wherein each R^{1j}, with j = 1-3 is independently selected from the group consisting of a hydrogen atom, a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, or a C_{1-20} hydrocarbyl radical unsubstituted or substituted by a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, a silyl radical of the formula:



(formula 4)

and a germanyl radical of the formula :



(formula 5)

wherein R^{2j} is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl and aryloxy radicals, each substituent R^{1j} or R^{2j} may be linked with another R^1 or R^2 to form a ring system,

and M represents a group 4 or group 5 metal ion

V represents the valency of the metal ion, being 3, 4 or 5

L_1, L_2, L_3, and L_4 represent a ligand or a group 17 halogen atom on M and may be equal or different,

k, l, m, n = 0,1, 2, 3, 4 with k+l+m+n+1=V, and

X represents a group 17 halogen atom.

This invention is supported by original claim 1 and in the Specification at the following locations: the Abstract; page 1 line 33 to page 2 line 18; page 3 line 27 to page 4 line 16; and page 6 lines 1-3.

Therefore, the invention as presently claimed is clearly supported by Appellants' disclosure as originally filed.

VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

A. Under 35 U.S.C. 103(a), was it proper to reject claims 1-5 and 11-15 as allegedly unpatentable over U.S. Patent 6,355,744 in view of CA 2,261,518?

VII. ARGUMENTS

Claims 1-5 and 11-15 should stand or fall together as one group.

35 U.S.C. 103 – Nonobviousness

A claimed invention is unpatentable if the differences between it and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art. *In re Kahn*, 78 USPQ2d 1329, 1334 (Fed. Cir. 2006) citing *Graham v. John Deere*, 148 USPQ 459 (1966). The *Graham* analysis needs to be made explicitly. *KSR v. Teleflex*, 82 USPQ2d 1385, 1396 (2007). It requires findings of fact and a rational basis for combining the prior art disclosures to produce the claimed invention. See id. ("Often, it will be necessary for a court to look to interrelated teachings of multiple patents . . . and the background knowledge

possessed by a person having ordinary skill in the art, all in order to determine whether there was an apparent reason to combine the known elements in the fashion claimed by the patent at issue"). The use of hindsight reasoning is impermissible. See id. at 1397 ("A factfinder should be aware, of course, of the distortion caused by hindsight bias and must be cautious of arguments reliant upon ex post reasoning"). Thus, a prima facie case of obviousness requires "some rationale, articulation, or reasoned basis to explain why the conclusion of obviousness is correct." *Kahn* at 1335; see *KSR* at 1396. A claim that is directed to a combination of prior art elements "is not proved obvious merely by demon-strating that each of its elements was, independently, known in the prior art." Id. Finally, a determination of prima facie obviousness requires a reasonable expectation of success. See *In re Rinehart*, 189 USPQ 143, 148 (C.C.P.A. 1976).

Claims 1-5 and 11-15 were rejected under Section 103(a) as allegedly being unpatentable over U.S. Patent 6,355,744 (cited as the '744 patent below) in view of Canadian Application 2,261,518 (cited as the CA'518 below).

In the final rejection, the Examiner alleges that it would have been obvious for a skilled artisan to employ CA'518's aminophosphonium halide to the '744 patent's phosphinimine ligand containing metal-organic compound preparation process. The Examiner further assumes that the aminophosphonium salt can be neutralized with a strong base as described on page 3, last paragraph of CA'518. The last paragraph on page 3 of CA'518 describes the use of bases such as NaOH, NaOMe and BuLi. The use of NaOH and NaOMe may appear to provide the phosphinimine at first glance. However, Appellants urge the Board to consider the fact that the use of MeOH is generally known to hydrolyze the phosphimine to the thermodynamically more stable

and undesired phosphinoxide under liberation of $MeNH_2$ (Evidence Appendix, Exhibit 1: Hawkeswood et al., 84 Dalton Trans. 2182-87, (2005), second reaction in scheme 2, submitted in the Amendment and Response of December 5, 2008). Similar hydrolyzing reactions may be expected when NaOH and NaOMe are used to neutralize the aminophosphonium salt. Therefore, there is no reasonable expectation of success shown by the Examiner that a phosphimine would be produced by reacting the aminophosphonium salt with bases such as NaOH, NaOMe and BuLi.

Appellants submit Grob (Evidence Appendix, Exhibit 2: Grob et al., 626 Zeitschrift fuer Anorganische und allgemeine Chemie 1065-72 (2000)) for the Board's consideration. Grob teaches that strong bases have to be extremely pure to prevent hydrolysis of phosphinimine. Further, KNPPh3 can only be made in an extremely dry environment (Grob, page 1071). Mixtures that contain phosphinoxide are difficult to purify. In particular, BuLi is a very strong base that complicates selective formation of the NH-phosphinimine caused by deprotonation of the NH-phosphinimine to the NLi-phosphinimide, resulting again in separation problems. For the reasons stated above, one of ordinary skill in the art would not have employed CA'518's aminophosphonium halide to the '744 patent's phosphinimine ligand containing metal organic compound preparation process since the prior art teaches against such as approach.

Furthermore, the Examiner's argument is based on the assumption that triethylamine is a stronger base than Y=N-H so that one would have expected that triethylamine would react with aminophosphonium halide to form phosphinimine and $(Et_3NH)^+Cl^-$. See, Final Office Action, sentence spanning pages 2 and 3 where the Examiner states, "Since triethylamine is a stronger base than Y=N-H, one would also

have expected that the most common amine base, triethylamine, to react with aminophosphonium halide to form phosphinimine and $(Et_3NH)^+Cl^-$ and further deprotonates the phosphinimine to provide Y=N- to react with the metal-organic reagent of formula 3 to prduce the metal-organic compound." Appellants respectfully disagree with the Examiner's contention. In fact, Clayden (Evidence Appendix, Exhibit 3: Clayden et al., Organic Chemistry, Oxford University Press 2001, submitted in the Amendment and Response of December 5, 2008) contradicts the Examiner's assumption, as can be derived from the pK values of Et_3N (see, Clayton, page 199, which shows a pK value of 10.8,) and guanidine (see, Clayton, page 202, pK value of 13.6). The pK value of guanidine is conservatively chosen as this is the lowest pK of the guanidine family. When substituted, the pK of the guanidine increases analogous to substitution of ammonia (pK increases from 9 to 11, pp. 198-99). The value of the used phosphinimines is comparable to that of substituted guanidines since they are isoelectronic. Because of this, one of ordinary skill in the art would not have expected that triethylamine to react with aminophosphonium halide to form phosphinimine and $(Et_3NH)^+Cl^-$.

For this reason, the combination of U.S. Patent 6,355,744 and CA 2,261,518 does not render the claimed invention obvious, inter alia, because there is no expectation that such a combination would cooperated in the manner proposed by the Examiner in the Final Office Action.

Appellants urge the Board to reverse the Section 103 rejection because their claimed invention would not have been obvious to one of ordinary skill in the art at the time it was made.

Conclusion

For the reasons discussed above, the Examiner's rejection is improper and they should be reversed by the Board. Appellants submit that the pending claims are in condition for allowance and earnestly solicit an early Notice to that effect.

Respectfully submitted,

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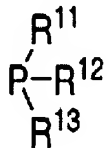
VIII. CLAIMS APPENDIX

1. A process for the preparation of a metal-organic compound, comprising at least one phosphinimine ligand, the process comprising contacting a HA adduct of a phosphinimine ligand compound according to formula 1 with a metal-organic reagent of formula 2 in the presence of at least 2 equivalents of a base, wherein HA represents an acid, of which H represents its proton and A its conjugate base,

with **Y=N-H** as formula 1,

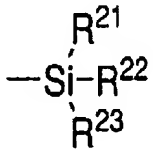
and $\mathbf{M^{v}(L_1)_k(L_2)_l(L_3)_m(L_4)_nX}$ as formula 2,

and wherein Y is defined by the formula :



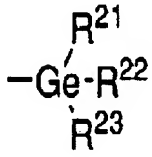
(formula 3)

wherein each R^{1j}, with j = 1-3 is independently selected from the group consisting of a hydrogen atom, a halogen atom, a C_{1-8}alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, or a C_{1-20} hydrocarbyl radical unsubstituted or substituted by a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, a silyl radical of the formula:



(formula 4)

and a germanyl radical of the formula :



(formula 5)

wherein R^{2j} is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl and aryloxy radicals, each substituent R^{1j} or R^{2j} may be linked with another R^1 or R^2 to form a ring system,

and M represents a group 4 or group 5 metal ion
V represents the valency of the metal ion, being 3, 4 or 5
L_1, L_2, L_3, and L_4 represent a ligand or a group 17 halogen atom on M and may be equal or different,
k, l, m, n = 0,1, 2, 3, 4 with k+l+m+n+1=V, and
X represents a group 17 halogen atom.

2. A process according to claim 1, wherein the base is an organic base, an inorganic base or a metal-organic base.

3. A process according to claim 1, wherein the organic base is an amine or a phosphane.

4. A process according to claim 1, wherein the organic base is a dialkylamine, a trialkylamine, amonoarylamine, diarylamine or a triarylamine.

5. A process according to claim 1, wherein the base is triethylamine, pyridine, tripropylamine, tributylamine, 1, 4-diaza-bicyclo [2.2. 2] octane, pyrrolidine or piperidine.

11. A process according to claim 1 wherein the reaction is carried out in an aprotic solvent.

12. A process according to claim 11, wherein the solvent is the base.

13. Process for the preparation of a polyolefin which comprises polymerizing an olefin monomer in the presence of a metal-organic compound made according to the process of claim 1, wherein the base is an olefin polymerisation compatible base, which metal-organic compound is activated anywhere in, or before polymerisation equipment.

14. Process according to claim 13, wherein the metal-organic compound is used without purification.

15. Process according to claim 13, wherein the metal-organic compound is formed in the polymerisation equipment.

IX. EVIDENCE APPENDIX

Exhibit 1

Hawkeswood et al., Dalton Trans. 2182-87, 84 (2005)

FULL PAPER

Dalton
www.rsc.org/dalton

Syntheses and reactions of the bis-boryloxide $O(Bpin)_2$ (pin = $O_2C_2Me_4$)

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The reaction of the phosphine oxides, $OPEt_3$ **1** and $OPn\text{-}Bu_3$ **2** with pinacolborane (HBpin) results in phosphine oxide reduction and the formation of O(Bpin)$_3$ **3**. In contrast, the phosphine oxide $OPn\text{-}Bu_3$ reacts with $HB(C_6F_5)_2$ or $B(C_6F_5)_3$ to give only the donor–acceptor adducts. Compound **3** reacts with $HNPt\text{-}Bu_2$ to give the phosphinimonium borate salt, $[t\text{-}Bu_2PNH_2][(Bpin(OBpin)_3]$ **6**, while reaction with Cp_2ZrMe_2 affords the species $Cp_2Zr(OBpin)_2$ **7**.

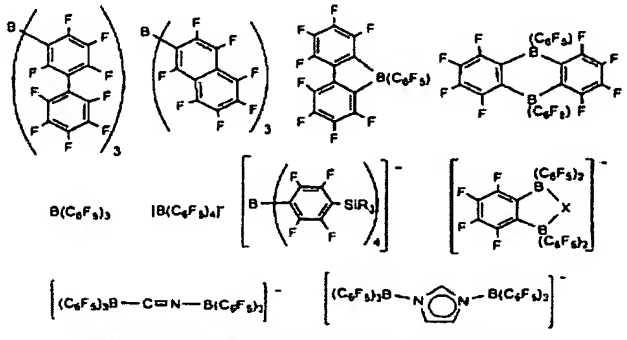
Introduction

The utility of methylalumoxane (MAO) as an activator for zirconocene olefin polymerization catalysts was discovered 25 years ago.[1] In this role MAO functions to alkylate early metal catalyst precursors and subsequently abstract an alkyl group to generate a coordinatively unsaturated metal cation and a weak or non-coordinating anion. The need to use typically 1000 equivalents of MAO to effect precatalyst activation as well as intellectual properties issues prompted researchers to seek alternative activators. Perhaps the most successful alternatives were developed by Exxon researchers in the 1980's and are based on Lewis acidic fluorinated-aryl-borane and the corresponding non-coordinating borates. More recently the research groups of Marks,[2-6] Piers,[10-17] and Bochmann[18] have developed a variety of more complex fluorinated B- and Al-based[10-18] Lewis acid activators and non-coordinating anions (Scheme 1). Nonetheless, the commercial use of many of creative developments are limited by the broad range of compounds defined in Exxon patents.[19-24] In our efforts, we have focused on the study of the fundamental reactivity of Group 13 compounds with the view that new reactivity will offer alternative avenues to activators or non-coordinating anions. To this end, we continue to explore the chemistry of boranes. In recent work, we have described the steric effects on the reaction pathways of phosphinimines and dialkoxyboranes.[25] Phosphinimines with sterically small substituents on P underwent reduction to the corresponding phosphine upon reaction with borane. In this manuscript, we probe the application of this finding to the reduction of phosphine oxides. The reaction of pinacolborane with phosphine oxides provides a facile and clean route to a bis-boryloxide which is readily converted to an unusual phosphinimonium bis-boryloxide-borate salt. Reactivity of the bis-boryloxide with dimethylzirconocene is also described and the implications regarding the potential utility of these compounds is considered.

Experimental

General data

All preparations were performed under an atmosphere of dry O_2-free N_2 employing either Schlenk-line techniques or a Vacuum Atmospheres glovebox. Solvents were purified employing Grubbs-type column systems manufactured by Innovative Technologies or were distilled from the appropriate drying agents under N_2. HBpin (pinacolborane), $Pn\text{-}Bu_3$, PEt_3, and N_3SiMe_3 were used as received from Sigma-Aldrich. Modified literature procedures were used to synthesize the phosphinimines.[26] ^1H, $^{11}B\{^1H\}$, ^{19}F, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance spectrometers. These spectrometers operate at either 300 or 500 MHz for ^1H NMR spectroscopy. Deuterated benzene and toluene were purchased from Cambridge Isotopes Laboratories, vacuum distilled from the appropriate drying agents and freeze–pump–thaw-degassed (3×). C_6D_6 was used to record the NMR spectra unless otherwise indicated. For ^1H and $^{13}C\{^1H\}$ NMR spectra, trace amounts of protonated solvents were used as reference and NMR chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra are referenced to 85% H_3PO_4, and $^{11}B\{^1H\}$ NMR spectra are referenced to $BF_3{\cdot}OEt_2$



Scheme 1 Some B-based activators and non-coordinating anions.

DOI: 10.1039/b504746a

and ^{31}F NMR spectra are referenced to CCl_3F. Combustion analyses were performed at the University of Windsor Chemical Laboratories.

Syntheses

Synthesis of OPR_3 (R = Et 1, *n*-Bu 2). These compounds were prepared in a similar fashion and thus one preparation is detailed. To neat $Et_3PNSiMe_3$ (4.0 g, 18.8 mmol) was added excess dry methanol (30 mL) *via* cannula at 25 °C. The resulting solution was refluxed for 16 h. The excess methanol, $MeOSiMe_3$ and $MeNH_2$ were removed *in vacuo* over a 6 h period. The product was crystallized from a pentane solution, dried *in vacuo* and recovered in 82% yield. 1: ^{1}H NMR (ppm): 1.16 (m, 6H, CH_2Me), 0.86 (m, 9H, Me); ^{31}P{^{1}H} NMR (ppm): 46.2; ^{13}C{^{1}H} NMR (ppm): 20.6 (d, PCH_2, $^1J_{P,C}$ = 65.8 Hz); 6.2 (s, Me). Calcd: H: 11.27%, C: 53.72%; Found: H: 11.16%, C: 53.58%. 2: 85% yield. ^{1}H NMR (ppm): 1.42 (m, 6H, PCH_2), 1.35 (m, 6H, $CH_2CH_2CH_3$), 1.23 (sextet, 6H, CH_2Me), $^3J_{H-H}$ = 4 Hz), 0.79 (t, 9H, Me, $^3J_{H-H}$ = 8 Hz); ^{31}P{^{1}H} NMR (ppm): 42.0; ^{13}C{^{1}H} NMR (ppm): 28.9 (d, PCH_2), $^1J_{P,C}$ = 32 Hz), 24.9 (d, $CH_2CH_2CH_3$, $^2J_{P,C}$ = 6 Hz), 24.7 (d, CH_2Me, $^1J_{P,C}$ = 2 Hz), 14.2 (s, Me). Calcd: H: 12.47%, C: 66.02%; Found: H: 12.49%, C: 65.98%.

Synthesis of $O(Bpin)_2$ 3.

Method (i). This method involves reaction of HBpin and one of **1**, **2** or $OPPh_3$, thus one such preparation is detailed. HBpin (0.344 mL, 2.73 mmol) was added *via* syringe to a solution of 1 (0.150 g, 1.13 mmol) in 25 mL of toluene. The solution was heated at reflux for 72 h. Toluene and Et_3P were removed *in vacuo* and the product was dissolved in minimal amounts of pentanes. A crystalline product precipitated at −33 °C and the supernatant was removed. The crystals of 3 were washed with cold pentanes, dried *in vacuo* and isolated in 92% yield. X-Ray quality crystals were obtained by recrystallization from pentanes at −33 °C.

Method (ii). $ONMe_3$ (0.129 g, 1.72 mmol) was added to a 100 mL Schlenk flask to which 40 mL of toluene was added. HBpin (0.5 mL, 3.45 mmol) was slowly added to the toluene slurry. The flask was put under static vacuum and stirred for 1 h. The solvent and NMe_3 were removed *in vacuo* and the resulting white solid was dried *in vacuo* for 16 h. The white solid was isolated in 96% yield. ^{1}H NMR (ppm): 1.00 (s, Me); ^{13}C{^{1}H} NMR (ppm): 83.3 (s, BOC), 25.0 (s, Me); ^{11}B{^{1}H} NMR (ppm): 21.6 ($\upsilon_{\frac{1}{2}}$ = 750 Hz). Calcd: H: 8.96%; C: 53.39%; Found: H: 8.85% C: 53.16%.

Synthesis of $(n\text{-}Bu_3PO)HB(C_6F_5)_3$ 4 and $(n\text{-}Bu_3PO)B(C_6F_5)_3$ 5. These compounds were prepared in a similar fashion and thus one preparation is detailed. To a solution of 2 (0.041 g, 0.188 mmol) in 3 mL of toluene, was added a solution of $HB(C_6F_5)_2$ (0.065 g, 0.188 mmol) in 3 mL of toluene. The solution was stirred for 72 h. The solvent was removed *in vacuo* and the product was obtained in 88% yield. 4: ^{1}H NMR (ppm): 1.30 (m, 6H, PCH_2), 1.00 (m, 12H, $CH_2CH_2CH_2Me$), 0.67 (t, 9H, Me, $^3J_{H-H}$ = 7 Hz), ^{31}P{^{1}H} NMR (ppm): 76.7; ^{13}C{^{1}H} NMR ($C_6D_5CD_3$, ppm): 25.1 (d, $^1J_{P,C}$ = 64 Hz), 24.0 (d, $^2J_{P,C}$ = 15 Hz), 23.2, 13.3; ^{11}B NMR (ppm): −12.7; ^{19}F NMR (ppm): −136.5, −159.7, −165.3. Calcd: H: 5.00%, C: 51.09%; Found: H: 4.88%, C: 51.01%. 5: 87% yield. ^{1}H NMR (ppm): 1.28 (m, 6H, PCH_2), 0.91 (m, 12H, $CH_2CH_2CH_3$), 0.62 (t, 9H, Me, $^3J_{H-H}$ = 7 Hz); ^{31}P{^{1}H} NMR (ppm): 71.8; ^{13}C{^{1}H} NMR (ppm): 148.8 (d(m), $^1J_{C-F}$ = 242 Hz, C_6F_5 (*o*-C)), 140.7 (d(m), $^1J_{C-F}$ = 249 Hz, C_6F_5 (*p*-C)), 138.0 (d(m), $^1J_{C-F}$ = 249 Hz, C_6F_5 (*m*-C)), 25.3 (d, PCH_2CH_2, $^1J_{P,C}$ = 66 Hz), 24.2 (d, $CH_2CH_2CH_3$), $^2J_{P,C}$ = 16 Hz), 23.3 (s, CH_2CH_2Me), 13.5 (s, CH_2Me); ^{11}B{^{1}H} NMR (ppm): −2.7 (br); ^{19}F NMR (ppm): −134.0, −157.7, −164.1. Calcd: H: 3.73%, C: 49.34%; Found: H: 3.72%, C: 48.82%.

Synthesis of $[t\text{-}Bu_2PNH_2][(Bpin(OBpin)_2]$ 6. Solid 3 (0.03 g, 0.11 mmol) was added to a solution of tBu$_2$PNH (0.024 g, 0.11 mmol) in 2 mL of pentane. A white solid precipitated from the pentane solution immediately. The mixture was stirred for 2 h and set aside to allow the solid to settle in the vial. The pentane soluble product (tBu$_2$PNBpin) was decanted off and the solid was washed twice with 2 mL of pentane. The product was dried *in vacuo*, resulting in a fine white powder in 80% yield. X-Ray quality crystals grew from a toluene solution. ^{1}H NMR (partial, ppm): 1.11 (d, 27H, t-Bu, $^1J_{P,H}$ = 12 Hz), 1.11 (br s, 36H, BOCMe); ^{31}P{^{1}H} NMR (ppm): 61.9; ^{13}C{^{1}H} NMR (partial, ppm): 39.5 (d, t-Bu, $^1J_{P,C}$ = 45 Hz), 29.6 (s, t-Bu), 26.5 (s, OCMe), 25.3 (s, OCMe). ^{11}B{^{1}H} NMR (ppm): 21.9, 9.3. Calcd: C: 57.08%, H: 10.39%, N: 2.21%; Found: C: 57.23%, H: 10.40%, N: 2.23%.

Synthesis of $Cp_2Zr(OBpin)_2$ 7. To a solution of 3 (0.106 g, 0.398 mmol) in 25 mL of toluene was added solid Cp_2ZrMe_2 (0.050 g, 0.199 mmol). The solution was refluxed for 16 h, followed by removal of toluene and MeBpin *in vacuo*. The solid was washed three times with pentane, dissolved in a minimal amount of toluene and stored at −33 °C. Crystalline material precipitated from the pentane solution, the supernatant was decanted off, and the product was dried *in vacuo*. A white crystalline solid was collected in 82% yield. X-Ray quality crystals were obtained by recrystallization from pentane at −33 °C. ^{1}H NMR (ppm): 6.15 (s, 10H, Cp), 1.14 (s, 24H, Me); ^{13}C{^{1}H} NMR (ppm): 114.3 (s, Cp), 81.3 (s, BOC), 25.4 (s, Me); ^{11}B{^{1}H} NMR (ppm): 19.2. Calcd: H: 6.75%, C: 52.08%; Found: H: 6.79%, C: 51.85%.

X-Ray data collection and reduction

Crystals were manipulated and mounted in capillaries in a glove box, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1329 frames with 10 second exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected ($4.5° < 2\theta < 45$–$50.0°$). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package. See Table 1 for crystallographic data.

Structure solution and refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[17] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on *F*. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the case of 3 the oxygen and chelate carbon atoms are disordered and were modelled with two orientations. For 7 disorder of the pinacolate chelates were modelled with two orientations of the O and C atoms in the chelate ring. In these cases the fractional atoms were refined isotropically and the hydrogen atoms for the pinacolate methyl groups were not included. C–H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined with the exception of the phosphinammonium protons in 6 which were located and refined. The locations of the largest peaks *in the final difference*

Table 1 Crystallographic data

Crystal	3	6	7
Molecular formula	$C_{12}H_{28}B_2O$	$C_{30}H_{33}B_3NO_4P$	$C_{23}H_{34}B_2O_4Zr$
Formula weight	269.93	631.23	507.33
a/Å	6.544(4)	10.752(3)	20.276(11)
b/Å	21.289(13)	13.737(4)	13.162(8)
c/Å	11.767(7)	14.181(4)	19.540(11)
α/°	90	94.422(6)	90
β/°	95.599(12)	104.550(6)	100.694(13)
γ/°	90	106.244(6)	90
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$
V/Å^3	1631.5(17)	1921.9(9)	5124(5)
D_{calc}/g cm^{-3}	1.099	1.091	1.315
Z	4	2	8
μ/mm^{-1}	0.081	0.114	0.461
θ range/°	1.91–23.27	1.50–23.32	1.85–23.29
Reflections	6727	8994	10468
Data $F_o^2 > 3\sigma(F_o^2)$	2340	5469	3687
Parameters	253	394	260
R^a	0.0974	0.0854	0.0942
R_w^b	0.2677	0.1554	0.2410
Goodness of fit	0.884	0.843	1.031

Data collected at 20 °C with Mo-Kα radiation ($\lambda = 0.71069$ Å). ^{a} $R = \sum(F_o - F_c)/\sum F_o$. ^{b} $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{\frac{1}{2}}$.

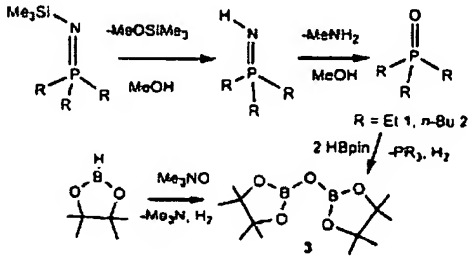
Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

CCDC reference numbers 266791–266793.

See http://www.rsc.org/suppdata/dt/b5/b504246a/ for crystallographic data in CIF or other electronic format.

Results and discussion

The alcoholysis of *N*-trimethylsilylphosphinimines is a firmly established route to *N*-H-phosphinimines.[26,29–32] While this reaction has been exploited extensively for the preparation of sterically bulky phosphinimines, the alcoholysis of less bulky phosphinimines to *N*-H-phosphinimines has been shown to be more sensitive, requiring the use of lower temperatures (−30 °C).[33] Herein, the analogous reactions of sterically unencumbered *N*-trimethylsilylphosphinimines at 25 °C are shown to result in the further transformation of *N*-H-phosphinimines to the corresponding phosphine oxides. In this fashion, the phosphine oxides, $OPEt_3$ 1 and $OPn\text{-}Bu_3$ 2 were obtained from the precursors $R_3PNSiMe_3$. The spectral data and elemental analyses confirmed the formulations of the products, 1 and 2. The impact of steric effects on the reaction pathways in the protonolyses is reminiscent of those recently described for the reactions of phosphinimines and pinacolboranes where small substituents prompted P–N bond cleavage. By analogy, the close approach of the sterically unencumbered electropositive P atom and an alcohol O atom presumably prompts the transformation to phosphine oxide (Scheme 2).



Scheme 2 Synthesis of 3.

The reactions of pinacolborane with the tertiary phosphine oxides 1, 2 or $OPPh_3$ were conducted in refluxing toluene for 72 h. $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectroscopy on the crude reaction mixture suggested the complete conversion to the corresponding tertiary phosphine and the formation of a single boron-containing compound 3. The boron-containing product was the same in each of these three reactions. In the case of the reaction of 1, the volatility of PEt_3 resulted in its facile removal by vacuum affording 3 cleanly in 92% yield. For the corresponding reaction of 2, removal of $Pn\text{-}Bu_3$ was effected *via* precipitation of 3 from pentane at −33 °C giving 3 in 65% yield. Finally in the case of the reaction of $OPPh_3$ filtration through Celite and removal of pentane yielded 3 in 75% yield. X-Ray crystallography (Fig. 1) and ^1H, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy were consistent with the formulation of 3 as $O(Bpin)_2$.

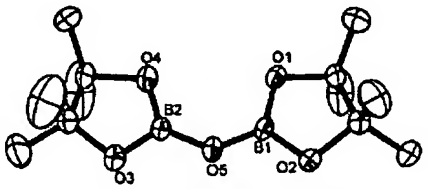


Fig. 1 ORTEP drawing of 3, 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity, one orientation of the disordered oxygens and chelate carbons are shown.

X-Ray crystallographic data for 3 confirmed the formulation and revealed that although there was significant disorder of the oxygen positions, the average B–O bond distances for the bridging oxygen atom was 1.36(2) Å while the B–O–B′ angle in 3 was found to average 136(2)°. These bond distances are similar to those observed in the related boryloxides $O(B(terphenyl)_2)_2$ (1.340(2) Å and 1.347(2) Å),[34] $O(B(Cl(N\text{-}iPr_2)_2)_2$ (1.367(3) Å and 1.367(3) Å),[35] $O(B(N_2(Ph)_2C))_2$ (1.365(4) Å and 1.370(4) Å)[36] and $O(B(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_2)_2$ (1.370(2) Å and 1.359(2) Å).[37] The disorder of the pinacolate chelate rings precludes direct comparison with the related species $(Bpin)_2$,[38] and $(Bpin)_2(OCMe_2CMe_2O)$.[39] The overall geometry of 3 is reminiscent of that recently reported for the species $HN(Bpin)_2$ where the B–N–B angle was found to be 132.9(3)°. However the B–O distances in 3 are significantly shorter than the B–N distance in $HN(Bpin)_2$ (1.419(6) Å).[38]

Several alternative syntheses of 3 were also uncovered. Prolonged reflux of pinacolborane in toluene (144 h), afforded numerous products including 3 which was isolated in 13% yield. An efficient route to 3 was shown to involve the reaction of Me_3NO with pinacolborane at 25 °C (Scheme 2), which affords 3 in 96% isolated yield. Similar reactions of trialkyl- or triarylboranes with amine oxides reported by Köster and Morita were shown to give trialkoxy- or triphenoxyboranes.[40] Similarly, reactions of species containing B–H bonds with amine-oxides afforded boryl-hydroxides. Thus, the reaction of pinacolborane and phosphine oxide or amine oxide is consistent with the proposed mechanism that results in reduction of the phosphine oxide or amine oxide and generation of the transient boryl-hydroxide species HOBpin which reacts immediately with excess borane to give 3. A similar mechanism involving transient boryl-hydroxides has been previously suggested for the oxidation of organoboranes with amine oxides.[40]

Other researchers have probed reductions of Group 15 and Group 16 elements with boranes. Some years ago, Köster and Morita showed that $OPPh_3$ is reduced by B_2Pr_4, BPr_3, BEt_2H and $B(NR_2)_3$,[41] although these reactions result in multiple boron-containing products. More recently, reduction of OPR_3 has been shown to occur in the presence of excess $BH_3{\cdot}SMe_2$, producing phosphine-borane adducts.[42,43] In addition, the deoxygenation of sulfoxides (R_2SO) to sulfides effected by reaction with

Table 1 Crystallographic data

Crystal	3	6	7
Molecular formula	$C_{12}H_{18}B_2O$	$C_{37}H_{33}B_3NO_3P$	$C_{17}H_{24}B_2O_4Zr$
Formula weight	269.93	631.23	507.33
a/Å	6.544(4)	10.752(3)	20.276(11)
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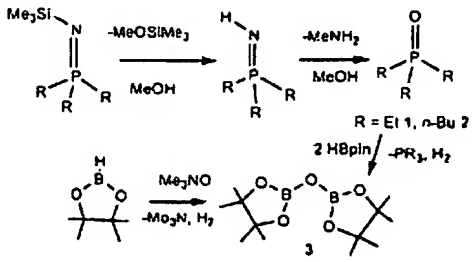

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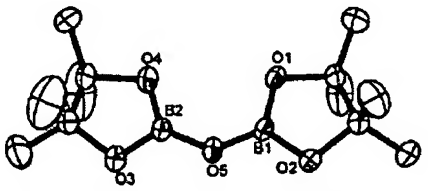

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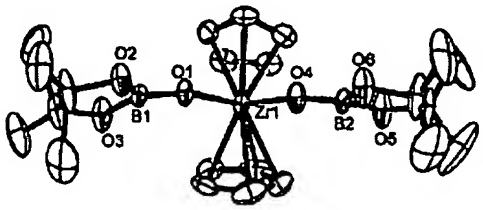
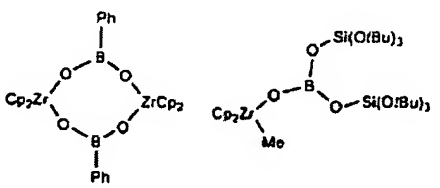


Fig. 3 ORTEP drawing of 7, 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity, one orientation of the disordered chelate carbons are shown. Selected distances (Å) and angles (°): Zr(1)–O(4) 2.011(9), Zr(1)–O(1) 2.025(8), O(1)–B(1) 1.291(16), O(2)–B(1) 1.311(17), O(3)–B(1) 1.400(17), O(4)–B(2) 1.280(15), O(5)–B(2) 1.360(16), O(6)–B(2) 1.357(16); O(4)–Zr(1)–O(1) 97.6(3), B(1)–O(1)–Zr(1) 156.0(9), B(2)–O(4)–Zr(1) 154.2(9), O(2)–B(1)–O(3) 108.6(13), O(5)–B(2)–O(6) 108.3(12).

Zr–O bond distances of 2.011(9) Å and 2.025(8) Å with a O–Zr–O' angle of 97.6(3)°. In comparison, the Zr–O bond distances and O–Zr–O' bond angles in the zirconocene–alkoxide species, $Cp_2Zr(\mu\text{-}OCH_2CMe_2CH_2O)_2ZrCp_2$ and $Cp_2Zr(\mu\text{-}OCH_2C_6H_4CH_2O)_2ZrCp_2$ are 1.945(6) Å, 1.946(6) Å, 101.4(3)° and 99.4(1)°, respectively.[55] The longer Zr–O bond length in 7 is consistent with the presence of the Lewis acidic boron center. The larger angles at Zr in the zirconocene–alkoxides may be an artifact of the macrocyclic nature of these complexes. The B–O bond distances were determined to be 1.291(16) Å and 1.280(15) Å with Zr–O–B bond angles of 156.0(9)° and 154.2(9)°. In addition, the Bpin units are canted with respect to the ZrO_2 plane by only 18.0° and 5.7° respectively. This geometry places the acceptor B p-orbital approximately orthogonal to a vacant a_1 molecular orbital on Zr, thus providing for strong Zr–O and B–O π-bonding and accounting for the increase in the angle at O.

Previous reports regarding the chemistry of boryloxides have been sparse over the last 15 years. The groups of Power, Chisholm, Gibson and Serwatowski have utilized boryloxide ligands to form metal complexes of Li, Co, Mn, Fe, Al, Zn and Cd.[56-62] In addition only two examples of Zr complexes containing boryloxide ligands have been reported. Balkwill *et al.* have described the bimetallic complexes $(Cp_2Zr(\mu^1\text{-}O_2BAr))_2$ (Ar = Ph, C_6H_3-2,4,6-Me_3, C_6F_5) (Scheme 5).[63] synthesized *via* reaction of Cp_2ZrMe_2 with $ArB(OH)_2$ generated *via* hydrolysis of $(OBAr)_3$. These macrocyclic species exhibit shorter average Zr–O (1.985(2) Å) bonds and longer average B–O (1.350(6) Å) bonds. At the same time, the Zr–O–B angles range from 141.8(2)° to 156.7(2)° for the derivatives with Ar = Ph, C_6H_3-2,4,6-Me_3. The upper limit of this range is similar to the Zr–O–B angles seen in 7, but presumably the macrocyclic nature of these complexes accounts for the lower end of this range. More recently, Tilley's group has also reported the structure of the related boryloxide derivative $Cp_2ZrMe(OB(OSi(O\text{-}t\text{-}Bu)_3)_2)$ (Scheme 5).[64] The Zr–O distance of 1.974(4) Å is slightly shorter than those in 7 while the bridging B–O bond distance and Zr–O–B angle are slightly larger at 1.329(3) Å and 160(2)°, respectively. These metric perturbations are consistent with the steric demands of the boryloxide substituents in $Cp_2ZrMe(OB(OSi(O\text{-}t\text{-}Bu)_3)_2)$.



Scheme 5 Known Zr–boryloxide species.

The facile formation of 7 from the reaction of Cp_2ZrMe_2 and 3 is thought to be initiated by interaction of the Lewis acidic B center with the Zr-bound methyl group. This prompts simultaneous formation of MeBpin and transfer of the boryloxide ligand to Zr. Presumably this process repeats to give 7. All attempts to intercept the intermediate in this process were unsuccessful. This chemistry reflects both the acidity of the B centers and the reactivity of the B–O bonds in 3. Thus, while the reactivity shown herein affords a new synthetic route to a B-based anion, the lability of the B–O bonds makes these boryloxides unsuitable for use as activators or non-coordinating anions. Efforts are underway to utilize this unique synthetic route to prepare related boryloxide salts in which the B–O bond strengths are enhanced by the introduction of electronically favorable and sterically demanding substituents. The results of these efforts will be reported in due course.

Acknowledgements

Financial support from NSERC of Canada, NOVA Chemicals Corporation is gratefully acknowledged. SH is grateful for the award of an OGS scholarship.

References

1 H. Sinn, W. Kaminsky, H. J. Vollmer and R. Woldt, *Angew. Chem.*, 1980, 92, 396.
2 M.-C. Chen and T. J. Marks, *J. Am. Chem. Soc.*, 2001, 123, 11803.
3 Y.-X. Chen, M. V. Metz, L. Li, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1998, 120, 6287.
4 L. Li and T. J. Marks, *Organometallics*, 1998, 17, 3996.
5 L. Li, C. L. Stern and T. J. Marks, *Organometallics*, 2000, 19, 3332.
6 T. J. Marks and Y.-X. Chen, in Organoborane complexes with metallocenes for polymerization catalysts, *US Pat.*, 629165, 2001.
7 T. J. Marks, L. Li, Y.-X. Chen, M. H. McAdon and P. N. Nickias, in Perfluoro group-substituted boron-containing activator for transition metal complex catalysts for polymerization of olefins, *WO Pat.*, 9906412, 1999.
8 M. H. McAdon, P. N. Nickias, T. J. Marks and D. J. Swartz, in Activators for transition metal complex catalysts for polymerization of olefins, *WO Pat.*, 9906413, 1999.
9 M. V. Metz, D. J. Schwartz, C. L. Stern, T. J. Marks and P. N. Nickias, *Organometallics*, 2002, 21, 4159.
10 L. D. Henderson, W. E. Piers, G. J. Irvine and R. McDonald, *Organometallics*, 2002, 21, 340.
11 K. Koehler, W. E. Piers, A. P. Jarvis, S. Xin, Y. Feng, A. M. Bravakis, S. Collins, W. Clegg, G. P. A. Yap and T. B. Marder, *Organometallics*, 1998, 17, 3557.
12 R. Roesler, B. J. N. Har and W. E. Piers, *Organometallics*, 2002, 21, 4300.
13 V. C. Williams, G. J. Irvine, W. E. Piers, Z. Li, S. Collins, W. Clegg, M. R. J. Elsegood and T. B. Marder, *Organometallics*, 2000, 19, 1619.
14 V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins and T. B. Marder, *J. Am. Chem. Soc.*, 1999, 121, 3244.
15 J. Zhou, S. J. Lancaster, D. A. Walker, S. Beck, M. Thornton-Pett and M. Bochmann, *J. Am. Chem. Soc.*, 2001, 123, 223.
16 T. J. Marks and Y.-X. Chen, in Synthesis and use of (polyfluoroaryl)fluoroanions of aluminum, gallium and indium as polymerization cocatalysts, *US Pat.*, 6130302, 2000.
17 T. J. Marks and Y.-X. Chen, in (Polyfluoroaryl)fluoroanions of aluminum, gallium, and indium of enhanced utility, uses thereof, and products based thereon, *US Pat.*, 6262200, 2001.
18 Y. Sun, M. V. Metz, C. L. Stern and T. J. Marks, *Organometallics*, 2000, 19, 1625.
19 S. M. Chranowski, M. J. Krause and F. Y.-K. Lo, in Catalyst for use in olefin polymerization or copolymerization, *WO Pat.*, 9722635, 1995.
20 D. J. Crowther, R. A. Fisher, J. A. M. Canich, G. G. Hlatky and H. W. Turner, in Transition metal complexes and their manufacture for olefin polymerization catalysts, *WO Pat.*, 19930701, 1994.
21 H. W. Turner, C. S. Speed, B. J. Folie, D. J. Crowther, J. F. Walzer, Jr., R. A. Fisher, and G. A. Vaughan, in *High temperature olefin polymerization process using metallocene catalyst*, WO, 9722635, 1997.
22 H. W. Turner, G. A. Vaughan, R. A. Fisher, J. F. Walzer, Jr., C. S. Speed, B. J. Folie, and D. J. Crowther, in High-temperature olefin polymerization process, *US Pat.*, 5767208, 1998.

23 D. J. Upton, J. A. M. Canich, G. G. Hlatky and H. W. Turner, in Supported ionic transition metal catalysts and their manufacture for olefin polymerization, *WO Pat.*, 9403506, 1994
24 J. F. Walzer, Jr., A. J. Dias, J. M. J. Frechet and S. B. Roscoe, in Polymeric supported catalysts for olefin polymerization, *WO Pat.*, 9855518, 1998.
25 S. B. Hawkeswood, P. Wei, J. Gauld and D. W. Stephan, *Inorg. Chem.*, 2005, **44**, in press.
26 D. W. Stephan, J. C. Stewart, F. Guerin, S. Courtenay, J. Kickham, E. Hollink, C. Beddie, A. Hoskin, T. Graham, P. Wei, R. E. v. H. Spence, W. Xu, L. Koch, X. Gao and D. G. Harrison, *Organometallics*, 2003, **22**, 1937.
27 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
28 S. Courtenay, C. M. Ong and D. W. Stephan, *Organometallics*, 2003, **22**, 818.
29 C. M. Ong, P. McKarns and D. W. Stephan, *Organometallics*, 1999, **18**, 4197.
30 K. Dehnicke and J. Straehle, *Polyhedron*, 1989, **8**, 707.
31 K. Dehnicke, M. Krieger and W. Massa, *Coord. Chem. Rev.*, 1999, **182**, 19.
32 K. Dehnicke and F. Weller, *Coord. Chem. Rev.*, 1997, **158**, 103.
33 L. Birkofer and S. M. Kim, *Chem. Ber.*, 1964, **97**, 2100.
34 I. Cynkier and N. Furmanova, *Cryst. Struct. Commun.*, 1980, **9**, 307.
35 W. Maringgele, M. Noltemeyer and A. Meller, *Organometallics*, 1997, **16**, 2276.
36 L. Weber, M. Schnieder, H.-G. Stammler, B. Neumann and W. W. Schoeller, *Eur. J. Inorg. Chem.*, 1999, 1193.
37 C. J. Cardin, H. E. Parge and J. W. Wilson, *J. Chem. Res. (S)*, 1983, 93.
38 H. Noth, Z. *Naturforsch., Teil B*, 1984, **39**, 1463.
39 S. A. Westcott, H. P. Blom, T. B. Marder, R. T. Baker and J. C. Calabrese, *Inorg. Chem.*, 1993, **32**, 2175.
40 R. Koester and Y. Morita, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 580.
41 R. Koester and Y. Morita, *Angew. Chem.*, 1965, **77**, 589.
42 G. Keglevich, T. Chuluunbaatar, K. Ludanyi and L. Toke, *Tetrahedron*, 2000, **56**, 1.
43 G. Keglevich, M. Fekete, T. Chuluunbaatar, A. Dobo, V. Harmat and L. Tke, *J. Chem. Soc., Perkin Trans. 1*, 2000, 4451.
44 D. J. Harrison, N. C. Tam, C. M. Vogels, R. F. Langler, R. T. Baker, A. Decken and S. A. Westcott, *Tetrahedron Lett.*, 2004, **45**, 8493.
45 J. Goubeau and H. Keller, *Z. Anorg. Allg. Chem.*, 1951, **267**, 1.
46 H. Noth and P. Schweizer, *Chem. Ber.*, 1964, **94**, 1464.
47 M. Komorowska, K. Niedenzu and W. Weber, *Inorg. Chem.*, 1990, **29**, 289.
48 D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 809.
49 D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492.
50 M. A. Beckett, D. S. Brassington, S. J. Coles and M. B. Hursthouse, *Inorg. Chem. Commun.*, 2000, **3**, 530.
51 M. A. Beckett, D. S. Brassington, M. E. Light and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 2001, 1768.
52 W. Clegg, A. J. Scott, F. J. Lawlor, N. C. Norman, T. B. Marder, C. Dai and P. Nguyen, *Acta Crystallogr., Sect. C.*, 1998, **54**, 1875.
53 W. Clegg, A. J. Scott, C. Dai, G. Lesley, T. B. Marder, N. C. Norman and L. Farrugia, *Acta Crystallogr., Sect. C*, 1996, **52**, 2545.
54 W. Clegg, A. J. Scott, M. R. J. Elsegood, T. B. Marder, C. Dai, N. C. Norman, E. G. Robins and N. L. Pickett, *Acta Crystallogr., Sect. C*, 1999, **55**, 733.
55 D. W. Stephan, *Organometallics*, 1990, **9**, 2718.
56 K. J. Weese, R. A. Bartlett, B. D. Murray, M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1987, **26**, 2409.
57 H. Chen, R. A. Bartlett, M. M. Olmstead, P. P. Power and S. C. Shoner, *J. Am. Chem. Soc.*, 1990, **112**, 1048.
58 M. H. Chisholm, K. Folting, S. T. Haubrich and J. D. Martin, *Inorg. Chim. Acta*, 1993, **213**, 17.
59 V. C. Gibson, S. Mastroianni, A. J. P. White and D. J. Williams, *Inorg. Chem.*, 2001, **40**, 826.
60 V. C. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *Polyhedron*, 1997, **16**, 2637.
61 R. Anulewicz-Ostrowska, S. Lulinski, J. Serwatowski and K. Suwinska, *Inorg. Chem.*, 2000, **39**, 5763.
62 S. Lulinski, S. Madura, J. Serwatowski and J. Zachara, *Inorg. Chem.*, 1999, **38**, 4937.
63 J. E. Balkwill, S. C. Cole, M. P. Coles and P. B. Hitchcock, *Inorg. Chem.*, 2002, **41**, 3548.
64 K. L. Fujdala, A. G. Oliver, F. J. Hollander and T. D. Tilley, *Inorg. Chem.*, 2003, **42**, 1140.

Exhibit 2

Grob et al., 626 Zeitschrift fuer Anorganische und allgemeine Chemie 1065-72 (2000)

Alkalimetall-Phosphaniminate. Neue Synthesen und die Kristallstrukturen von $[RbNPPh_3]_6$ und $[CsNPPh_3]_4$

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Professor Gerd Becker zum 60. Geburtstag gewidmet

Inhaltsübersicht. Die Alkalimetall-Phosphaniminate $MNPPh_3$ mit M = Na, K, Rb, Cs werden durch Reaktion von Ph_3PI_2 mit den Alkalimetallamiden in flüssigem Ammoniak hergestellt und durch Extraktion mit Toluol in reiner Form erhalten. Das Ethylderivat $KNPEt_3$ wird analog hierzu aus Et_3PBr_2 hergestellt und mit Hexan in reiner Form extrahiert.

Einkristalle der Phosphaniminate von Rubidium und Caesium werden aus Toluol bzw. Toluol/Hexan erhalten und durch Kristallstrukturanalysen charakterisiert.

$[RbNPPh_3]_6 \cdot 4^1/_2$ Toluol (1): Raumgruppe $P\bar{1}$, Z = 2, Gitterkonstanten bei 193 K: a = 1525.5(2); b = 1902.9(2); c = 2178.3(2) pm; α = 95.435(12)°; β = 91.145(12)°; γ = 90.448(12)°; R_1 = 0.0529. Die Verbindung hat die Struktur eines Doppelwürfels, dessen N-Atome der gemeinsamen Rb_2N_2-Fläche trigonal-bipyramidal von vier Rb-Atomen und dem P-Atom der $(NPPh_3^-)$-Gruppe umgeben sind.

$[CsNPPh_3]_4 \cdot 2$ Toluol $\cdot 3^3/_4$ Hexan (2a): Raumgruppe $Fd\bar{3}$, Z = 8, Gitterkonstanten bei 123 K: a = b = c = 2679.7(1) pm; R_1 = 0.0405.

$[CsNPPh_3]_4 \cdot 2$ Toluol (2b): Raumgruppe $P2_1/n$, Z = 4, Gitterkonstanten bei 193 K: a = 1418.9(1); b = 2258.9(1); c = 2497.6(1) pm; β = 91.055(6)°; R_1 = 0.0278. Beide Caesiumverbindungen bilden Cs_4N_4-Heterokubangerüste, die sich durch ihre Packung und durch die Bindungswinkel an den Cs- und N-Atomen unterscheiden.

Alkali Metal Phosphoraneiminates. New Syntheses and Crystal Structures of $[RbNPPh_3]_6$ and $[CsNPPh_3]_4$

Abstract. The alkali-metal phosphoraneiminates $MNPPh_3$ with M = Na, K, Rb, Cs have been synthesized by reactions of Ph_3PI_2 with the alkali-metal amides in liquid ammonia and were obtained as pure samples by subsequent extraction with toluene. The ethyl derivative $KNPEt_3$ has been prepared by an analogous route from Et_3PBr_2 and extraction with hexane.

Single crystals of the phosphoraneiminates of rubidium and cesium are obtainable by crystallization from toluene and toluene/hexane, respectively. They were suitable for crystal structure determinations.

$[RbNPPh_3]_6 \cdot 4^1/_2$ toluene (1): space group $P\bar{1}$, Z = 2, lattice dimensions at 193 K: a = 1525.5(2); b = 1902.9(2); c = 2178.3(2) pm; α = 95.435(12)°; β = 91.145(12)°; γ = 90.448(12)°; R_1 = 0.0529. The compound forms a Rb_6N_6 skeleton of a double cube with a common face of two rubidium and two nitrogen atoms, the latter being fivefold coordinated by four rubidium atoms and the phosphorus atom.

$[CsNPPh_3]_4 \cdot 2$ toluene $\cdot 3^3/_4$ hexane (2a): space group $Fd\bar{3}$, Z = 8, lattice dimensions at 123 K: a = b = c = 2679.7(1) pm; R_1 = 0.0405.

$[CsNPPh_3]_4 \cdot 2$ toluene (2b): space group $P2_1/n$, Z = 4, lattice dimensions at 193 K: a = 1418.9(1); b = 2258.9(1); c = 2497.6(1) pm; β = 91.055(6)°; R_1 = 0.0278. Both cesium compounds form Cs_4N_4 heterocubane structures which are different by means of the packing and by different bond angles at the cesium and nitrogen atoms.

Keywords: Alkali metal; Phosphorane iminates; Crystal structures

1 Einleitung

Zur Synthese der zahlreich bekannten Phosphaniminato-Derivate [M]-NPR_3 von Hauptgruppenelementen [1] und Übergangsmetallen [2] dienen vor allem Umsetzungen von Halogeniden, Oxiden und Oxidhalogeniden mit silylierten Phosphaniminen Me_3SiNPR_3. Erst in jüngster Zeit wurden auch lithiierte Phosphaniminate $LiNPR_3$ als Metathese-Reagentien erfolgreich bei Reaktionen mit Übergangsmetallhalogeniden eingesetzt [3, 4]. Bei Versuchen zur Herstellung von Phosphaniminato-Komplexen der Seltenerdelemente erwies sich das präparativ leicht in reiner Form zugängliche $LiNPPh_3$ [6] jedoch als nur bedingt geeignet. So führte beispielsweise die Reaktion mit den Cyclooctatetraenid-Komplexen $[Ln(C_8H_8)Cl(THF)_2]_2$ (Ln = Ce, Sm) nur unter Addition zu den Komplex-Aggregaten $[Ln(C_8H_8)Li_3Cl_2(NPPh_3)_2(THF)_3]$ mit

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Heterocubanstruktur [6]. Substitutions-Reaktionen mit $LiNPPh_3$ ließen sich nur unter Anwendung drastischer Bedingungen mit den Cyclopentadienid-Komplexen $[LnCp_2Br]_2$ (Ln = Y, Dy, Er, Yb) erreichen [7]. Wir waren daher an der Synthese möglichst reiner Phosphaniminate der schwereren Alkalimetalle interessiert, zumal die auf der Basis von Phosphaniminen $HNPR_3$ beruhenden Verfahren wegen der Schwierigkeiten, dieses in reiner Form zu erhalten, sehr problematisch sind [8].

2 Ergebnisse

Die Synthese von $NaNPPh_3$ verläuft am besten durch Umsetzung des strukturell wohlcharakterisierten Ph_3PI_2 [9, 10] mit Natriumamid in einer Suspension von Toluol, dem man als Lösungsvermittler etwa ein Molprozent Tetrahydrofuran beigesetzt hat, nach Gleichung (1) innerhalb von drei Tagen bei 20 °C.

$$Ph_3PI_2 + 3\,NaNH_2 \rightarrow NaNPPh_3 + 2\,NH_3 + 2\,NaI \qquad (1)$$

Nach Filtration von Natriumiodid kann Natriumtriphenylphosphaniminat durch Einengen des Filtrats und Fällen mit Hexan als blaß-beiges, sehr feuchtigkeitsempfindliches Kristallpulver mit über 80% Ausbeute erhalten werden.

Reaktion (1) verläuft offensichtlich in drei Schritten (1 a–1 c).

$$Ph_3PI_2 + NaNH_2 \rightarrow [Ph_3PNH_2]^+I^- + NaI \qquad (1\,a)$$

$$[Ph_3PNH_2]^+I^- + NaNH_2 \rightarrow Ph_3PNH + NaI + NH_3 \qquad (1\,b)$$

$$Ph_3PNH + NaNH_2 \rightarrow Ph_3PNNa + NH_3 \qquad (1\,c)$$

Die Teilreaktion (1 a) ist im wesentlichen bereits nach einer Stunde beendet, was man am Farbwechsel von gelb nach beige erkennt. Die Bildung des $[Ph_3PNH_2]^+$-Ions läßt sich anhand des ^{31}P-NMR-Signals bei 37.9 ppm in THF nachweisen. Vergleichswerte sind für $[Ph_3PNH_2]Cl$ in CH_2Cl_2 $\delta = 35{,}5$ [11], in DMSO-d_6 $\delta = 36{,}2$ [12] und für $[Ph_3PNH_2]Br$ in $CHCl_3/CH_3OH$ $\delta = 35.7$ [13]. Unterbricht man die Reaktion (1) ein zweites Mal nach etwa 1–2 Tagen, so lassen sich nach Filtration gelbe Einkristalle des Molekül-Komplexes $[NaI(HNPPh_3)_3]$ isolieren, in denen nach der Kristallstrukturanalyse das Natriumatom tetraedrisch von dem Iodatom und den N-Atomen der drei Phosphanimin-Moleküle koordiniert ist [8]. Dies beweist die Bildung des nach (1 b) entstandenen Intermediats $HNPPh_3$.

Zur Synthese der entsprechenden Phosphaniminate $MNPPh_3$ mit M = Kalium, Rubidium und Caesium ist es zweckmäßig, die Umsetzung gemäß Gleichung (1) in flüssigem Ammoniak bei –78 °C auszuführen. Hierbei erzeugt man das benötigte Alkalimetall-Amid durch Zugabe des entsprechenden Metall-Hydrids zu flüssigem Ammoniak und fügt nach beendeter Wasserstoffentwicklung Ph_3PI_2 hinzu. Die Reaktionen sind dann bereits nach drei Stunden beendet. Die reinen Alkalimetall-Phosphaniminate erhält man anschließend durch Extraktion mit Toluol, wobei sich nach dem Einengen der Lösungen gelbe Einkristalle erhalten lassen, die Einschlüsse definierter Mengen Toluol aufweisen (s. u.). Beim längeren Evakuieren werden die eingeschlossenen Lösungsmittel-Moleküle vollständig abgegeben. Der hier beschriebene Syntheseweg für Alkalimetall-Phosphaniminate ist nach unseren Erfahrungen weitgehend allgemein anwendbar. So haben wir auch die Derivate $KNP(p\text{-Tolyl})_3$ und $NaNP(o\text{-MeOPh})_3$ in reiner Form herstellen können. Schließlich kann man auch anstelle der Triorganodiiodide R_3PI_2 die leicht zugänglichen Dibromide R_3PBr_2 einsetzen, was wir anhand der glatt verlaufenden Synthese von $KNPEt_3$ geprüft haben. Diese Verbindung löst sich sehr leicht in vielen organischen Lösungsmitteln, darunter sogar in Hexan. Mit Feuchtigkeit, protonenaktiven Lösungsmitteln und mit Halogenkohlenwasserstoffen, sogar Fluoriden, reagiert $KNPEt_3$ außerordentlich stürmisch.

Tabelle 1 ^{31}P-NMR-Daten und Lage der PN-Valenzschwingungen in den Alkalimetall-Phosphaniminaten

	^{31}P-NMR-Resonanzen/ppm			ν PN/cm^{-1}
	THF	Toluol	DME	Nujol
$[LiNPPh_3]_6$ [14]	–4.6			[14] 1193
$[NaNPPh_3]_6$ [a]	–11.2	–9.4	–10.2	[a] 1186
$[KNPPh_3]_6$ [a]	–15.7	–13.2	–14.8 (br)	[15] 1179/1164
$[RbNPPh_3]_6$ [a]	–24.0	–21.8		[a] 1186/1165
$[CsNPPh_3]_6$ [a]	–24.1	–21.5	–22.5	[a] 1183
$[NaNP(o\text{-MeOPh})_3]_n$ [a]	–22.0	–15.3		[a] 1182/1165
$[KNP(p\text{-Tolyl})_3]_n$ [a]		–19.7		[a] 1180/1163
$[KNPEt_3]_n$ [a]		–19.0		[a] 1164

[a] diese Arbeit

In den IR-Spektren weisen die Alkalimetall-Phosphaniminate mit Arylresten am Phosphoratom eine starke, nur wenig von dem Alkalimetall-Atom beeinflußte PN-Valenzschwingung bei etwa 1180 cm^{-1} auf, die mitunter in ein Dublett aufgespalten ist (Tabelle 1). Ein Kopplungseinfluß durch die Masse der Alkalimetall-Atome ist somit vernachlässigbar klein. In dem Ethyl-Derivat $[KNPEt_3]_n$ tritt νPN mit 1164 cm^{-1} nur wenig längerwellig auf. In den ^{31}P-NMR-Spektren der Alkalimetall-Phosphaniminate (Tabelle 1) tritt unabhängig von den unterschiedlichen Festkörperstrukturen (s. u.) jeweils nur ein Resonanzsignal auf, das vom Lithium- bis zum Caesium-Derivat bei den Phenylverbindungen schrittweise zu höherem Feld verschoben wird. Im Vergleich mit den ^{31}P-NMR-Spektren aller anderen Phosphaniminato-Komplexe von Haupt- und Nebengruppen-Elementen [1, 2] stellen die Alkalimetall-Derivate die Verbindungen mit den am stärksten abgeschirmten Phosphoratomen dar. Hierin spiegelt sich der stark ionische Bindungscharakter wider. Auffällig ist der nur geringe Einfluß des Lösungsmittels auf die Lage des Resonanzsignals (Tabelle 1). Dies ist ein Hinweis auf einen

Tabelle 2 Kristalldaten und Angaben zu den Kristallstrukturbestimmungen

	$[RbNPPh_3]_6 \cdot 4^1/_2 C_7H_8$ (1)	$[CsNPPh_3]_4 \cdot 2 C_7H_8 \cdot 3^3/_4 C_6H_{14}$ (2a)	$[CsNPPh_3]_4 \cdot 2 C_7H_8$ (2b)
Gitterkonstanten	a = 1525.5(2) α = 95,435(12)° b = 1902.9(2) β = 91.145(12)° c = 2178.3(2) pm γ = 90,448(12)°	a = b = c = 2679.7(1)	a = 1418,9(1) b = 2258,9(1) β = 91,055(6)° c = 2497.6(1) pm
Zellvolumen/Å^3	V = 6293.4(11)	V = 19243.0(17)	V = 8003.7(7)
Zahl der Formeleinheiten pro Zelle	Z = 2	Z = 8	Z = 4
Dichte (ber.)/g · cm^{-3}	1.364	1.480	1.511
Kristallsystem, Raumgruppe	triklin, $P\bar{1}$	kubisch, $Fd\bar{3}$	monoklin, $P2_1/n$
Meßgerät	STOE IPDS		
Strahlung	MoKα (Graphit-Monochromator)		
Meßtemperatur	193(2) K	123(2) K	193(2) K
Zahl der Reflexe zur Gitterkonstantenberechnung	8000	8000	8000
Meßbereich	θ = 1.88–22.50°	θ = 2.15–24.04°	θ = 1.87–25.99°
Zahl der gemessenen Reflexe	31866	24367	71986
Zahl der unabhängigen Reflexe	15646 [R_{int} = 0.0883]	1282 [R_{int} = 0.0679]	15351 [R_{int} = 0.0525]
Zahl der beobachteten Reflexe mit $F_o > 4\sigma(F_o)$	8000	603	10401
Korrekturen	Lorentz- und Polarisationsfaktor, empirische Absorptionskorrektur		
	μ(MoKα) = 24.43 cm^{-1}	μ(MoKα) = 16.20 cm^{-1}	μ(MoKα) = 19.33 cm^{-1}
Bemerkungen	H-Atomlagen in berechneten Positionen		
Strukturaufklärung	Direkte Methoden		
Verfeinerung	Vollmatrix gegen F^2		
Anzahl der Parameter	1356	88	1125
Verwendete Rechenprogramme	SHELXS-97 [27], SHELXL-97 [27], SHELXTL [28], STOE IPDS-Software		
Atomformfaktoren, $\Delta f'$, $\Delta f''$	Internationale Tabellen, Vol. C		
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0529	0.0405	0.0278
wR_2 (alle Daten)	0.1228	0.1281	0.0630

Erhalt der im festen Zustand vorliegenden oligomeren Strukturen in Lösung. Beim Wechsel der Donor-Lösungsmittel THF und DME zu Toluol ist in allen Fällen eine um wenige ppm zu tieferen Feld verschobene Resonanz festzustellen. Dies könnte ein Hinweis auf die etwas schwächere Solvatationsstärke des Toluols sein.

3 Kristallstrukturanalysen

Tabelle 2 enthält die kristallographischen Daten und Angaben zu den Strukturlösungen, in den Tabellen 3 bis 5 sind die Bindungslängen und -winkel enthalten.[1)]

Kristallstruktur-Analysen von Alkalimetall-Phosphaniminaten liegen vor von $[LiNPPh_3]_6 \cdot 5THF$ [6] und von $[NaNPPh_3]_6 \cdot$Toluol [16], die beide hexagonal-prismatische M_6N_6-Gerüste aufweisen. Dagegen hat die Kalium-Verbindung $[KNPPh_3]_6 \cdot 4 C_7H_8$ [15] die Struktur eines aus den Gerüstatomen Kalium und Stickstoff gebildeten Doppelwürfels mit einer gemeinsamen K_2N_2-Fläche. Sie läßt sich topologisch aus der hexagonal-prismatischen Anordnung von Lithium- und Natrium-Derivat durch ein paarweises Zusammenrücken je zweier MN-Gerüstatome verstehen. Dieser Strukturtyp wird auch von der Rubidiumverbindung realisiert (s.u.). Überraschenderweise tritt nun beim Caesium-Derivat ein erneuter Strukturwechsel zur tetrameren Einheit $[CsNPPh_3]_4$ mit Heterokuban-Anordnung der Gerüstatome Caesium und Stickstoff ein. Der Heterokuban-Strukturtyp wird auch bei dem Gemischtligand-Komplex $[(LiNPPh_3 \cdot LiBr)_2 \cdot 4THF]$ [17] angetroffen, in dem die Würfelecken durch vier Lithium-, zwei Stickstoff- und zwei Bromatome besetzt sind.

3.1 $[RbNPPh_3]_6 \cdot 4^1/_2 C_7H_8$ (1)

1 ist isotyp mit der entsprechenden Kaliumverbindung $[KNPPh_3]_6 \cdot 4 C_7H_8$ [15], die einen etwas geringeren Anteil eingelagerter Toluol-Moleküle enthält. Von diesen haben in beiden Verbindungen nur jeweils zwei Toluol-Moleküle bindende Kontakte mit je einem der Metallatome der hexameren Einheiten $[MNPPh_3]_6$ (M = K, Rb). Alle Toluol-Moleküle sind fehlgeordnet, ihre Ortskoordinaten ließen sich unter Anwendung von Splitmethoden zufriedenstellend verfeinern.

Die Struktur von $[RbNPPh_3]_6 \cdot 4^1/_2 C_7H_8$ enthält zwei symmetrieunabhängige hexamere Moleküle, die sich nur wenig voneinander unterscheiden. Ihre Gerüstatome bilden einen zentrosymmetrischen Doppelwürfel mit einer gemeinsamen Rb_2N_2-Fläche, die ebenso wie alle anderen Rb_2N_2-Viereckflächen planar sind (Abbildung 1 und 2). Die Stickstoffatome N(1, 1A) der gemeinsamen Fläche haben Koordinationszahl fünf (ein P- und vier Rb-Atome) mit trigonal-bipyramidaler Anordnung, wobei die Achse Rb(1)–N(1)–Rb(2A) und die symmetrieäquivalente

[1)] Die kristallographischen Daten (ohne Strukturfaktoren) wurden als „supplementary publication no. CCDC-139049 (1), 139050 (2a) und 139051 (2b)" beim Cambridge Crystallographic Data Centre hinterlegt. Kopien der Daten können kostenlos bei CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk), Großbritannien, angefordert werden.

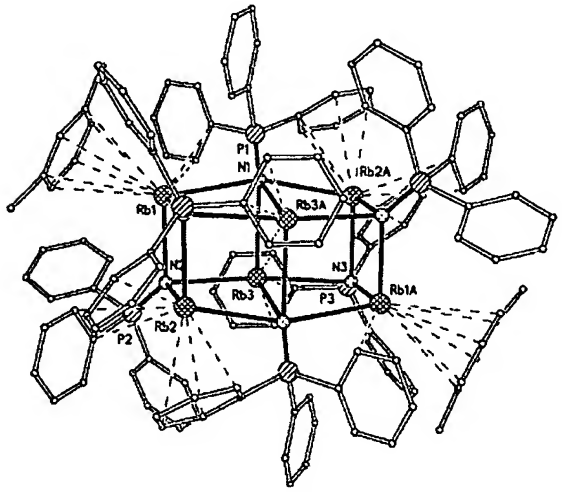

Abb. 1 Molekülstruktur von $[RbNPPh_3]_6$ mit der Darstellung der Fehlordnung der beiden an Rb(1) und Rb(1 A) assoziierten Toluol-Moleküle.

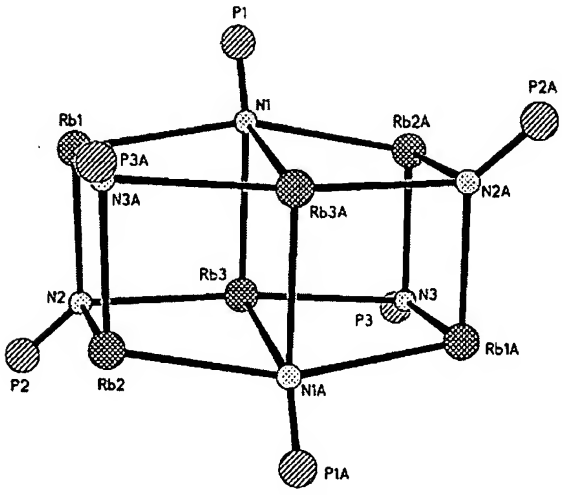

Abb. 2 Ansicht des Polyeders des von den Gerüstatomen Rb, N und P in der Struktur von 1 aufgespannten Doppelwürfels.

Achse mit einem Bindungswinkel von 161,3° merklich von der Linearität abweicht. Die von N(1) bzw. N(1 A) ausgehenden Rb–N-Abstände sind mit etwa 307 pm wegen der größeren Koordinationszahl deutlich größer als alle anderen Rb–N-Bindungen, die Abstände zwischen 279,5 und 288,4 pm aufweisen (Tabelle 3). Interessant ist, daß die axial angeordneten Rubidium-Atome an N(1) keine längeren Rb–N-Abstände realisieren als die äquatorialen Rb-Atome, was als ein Hinweis auf die stark polaren Bindungsbeziehungen zwischen den Rubidium-Ionen und den N-Atomen der Phosphaniminto-Gruppen ($NPPh_3^-$) gelten kann. Dies paßt auch zu den kurzen Abständen N(1)–P(1) bzw. N(1 A)–

Tabelle 3 Ausgewählte Bindungslängen/pm und -winkel/° in $[RbNPPh_3]_6 \cdot 4\,^1/_2$ Toluol (1)

Rb(1)–N(1)	307.1(6)	Rb(2)···C(14 A)	321.3(9)
Rb(1)–N(2)	279.5(7)	Rb(2)···C(15 A)	358.3(9)
Rb(1)–N(3 A)	282.0(6)	Rb(2)···C(18 A)	345.3(8)
Rb(1)···C(1)	367.6(8)	Rb(2)···C(31)	358.4(8)
Rb(1)···C(2)	353.2(8)	Rb(2)···C(32)	346.0(8)
Rb(1)···C(501)	354(1)	Rb(2)···C(44 A)	350.2(9)
Rb(1)···C(502)	367(1)	Rb(3)–N(1)	310.0(7)
Rb(1)···C(503)	370(1)	Rb(3)–N(1 A)	303.6(6)
Rb(1)···C(504)	364(1)	Rb(3)–N(2)	288.4(6)
Rb(1)···C(505)	345(1)	Rb(3)–N(3)	313.2(6)
Rb(1)···C(506)	341(1)	Rb(3)···C(49)	336.3(8)
Rb(2)–N(1 A)	303.3(6)	Rb(3)···C(50)	349.1(9)
Rb(2)–N(2)	288.1(6)	Rb(3)···C(54)	354.5(9)
Rb(2)–N(3 A)	282.9(7)	N(1)–P(1)	152.9(7)
Rb(2)···C(13 A)	314.8(8)	N(2)–P(2)	153.1(6)
		N(3)–P(3)	154.0(7)
N(1)–Rb(1)–N(2)	93.8(2)	Rb(1)–N(1)–Rb(2 A)	161.3(2)
N(1)–Rb(1)–N(3 A)	93.4(2)	Rb(1)–N(1)–Rb(3 A)	86.8(2)
N(2)–Rb(1)–N(3 A)	96.2(2)	Rb(1)–N(1)–Rb(3)	82.6(2)
N(1 A)–Rb(2)–N(2)	93.8(2)	Rb(2 A)–N(1)–Rb(3)	80.3(2)
N(1 A)–Rb(2)–N(3 A)	102.2(2)	Rb(2 A)–N(1)–Rb(3 A)	82.5(2)
N(2)–Rb(2)–N(3 A)	94.1(2)	Rb(3)–N(1)–Rb(3 A)	78.1(2)
N(1)–Rb(3)–N(2)	91.4(2)	Rb(1)–N(2)–Rb(2)	84.6(2)
N(1 A)–Rb(3)–N(2)	93.7(2)	Rb(1)–N(2)–Rb(3)	91.6(2)
N(1)–Rb(3)–N(1 A)	101.9(2)	Rb(2)–N(2)–Rb(3)	87.9(2)
N(1)–Rb(3)–N(3)	94.2(2)	Rb(1 A)–N(3)–Rb(2 A)	85.2(2)
N(1 A)–Rb(3)–N(3)	88.1(2)	Rb(1 A)–N(3)–Rb(3)	89.5(2)
N(2)–Rb(3)–N(3)	173.7(2)	Rb(2 A)–N(3)–Rb(3)	83.0(2)
Rb(1)–N(1)–P(1)	99.4(3)	Rb(3)–N(2)–P(2)	131.6(4)
Rb(3)–N(1)–P(1)	148.4(4)	Rb(1 A)–N(3)–P(3)	157.0(4)
Rb(3 A)–N(1)–P(1)	133.5(4)	Rb(2 A)–N(3)–P(3)	114.6(4)
Rb(1)–N(2)–P(2)	133.5(3)	Rb(3)–N(3)–P(3)	104.0(3)
Rb(2)–N(2)–P(2)	109.4(3)		

P(1 A) von 152.9 pm, die trotz Koordinationszahl fünf an N(1) nicht länger sind als an N(2) und N(3) (Tab. 3). Sie sind zudem vergleichsweise sehr kurz, wenn man den allgemein für P=N-Doppelbindungen angesehenen Bereich von 155–164 pm [18] berücksichtigt. Fünffach koordinierte N-Atome mit nitridischem Charakter wurden gelegentlich schon beobachtet; Beispiele sind $[Me_2Si(LiNBu^t)_2]_2$ [19] mit dodekaedrischem Li_4N_4-Gerüst und $[Na_{12}(NMe_2)_{12}(TMEDA)_4]$ [20], dessen hexamere Baueinheit $[NaNMe_2]_6$ topologisch verwandt ist mit $[RbNPPh_3]_6$.

Alle Rubidium-Atome in $[RbNPPh_3]_6 \cdot 4\,^1/_2C_7H_8$ haben bindende Wechselwirkungen mit Phenylgruppen der ($NPPh_3^-$)-Einheiten, die beiden Atome Rb(1, 1 A) zusätzlich mit je einem der eingelagerten Toluol-Moleküle (Abb. 1). Wie die in Tabelle 3 zusammengestellten Rb···C-Kontaktabstände zeigen, gibt es keine auf die C_6-Ringmitten von Phenylringen oder die Toluol-Moleküle zentrierten Bindungsbeziehungen. Nach allen Erfahrungen [21] können die hier beobachteten Rb···C-Abstände als schwach bindend angesehen werden.

3.2 *$[CsNPPh_3]_4 \cdot 2$ Toluol $\cdot 3\,^3/_4$ Hexan (2 a)*

In der Struktur von **2 a** bilden die Caesium- und die Stickstoffatome der tetrameren Moleküleinheit $[CsNPPh_3]_4$ ein regelmäßiges Heterokuban-Gerüst,

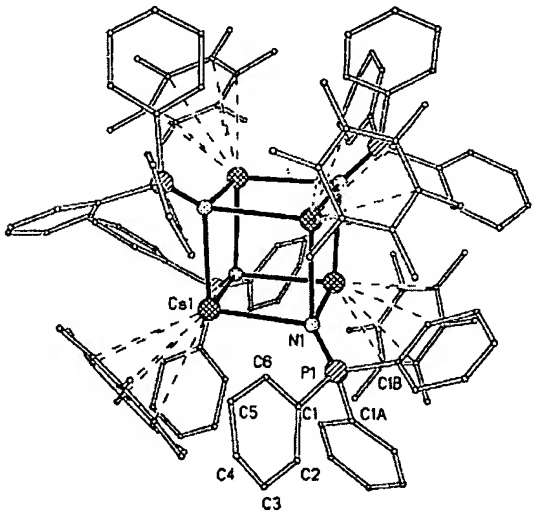

Abb. 3 Molekülstruktur von $[CsNPPh_3]_4 \cdot 2$ Toluol in **2a** mit der Darstellung der Fehlordnung der an die Caesium-Atome assoziierten Toluol-Moleküle.

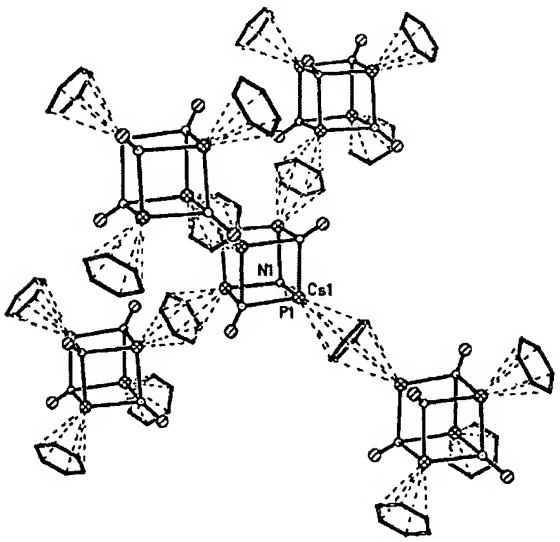

Abb. 4 Ausschnitt aus der durch die Brückenfunktion der Toluol-Moleküle vermittelten dreidimensionalen supramolekularen Struktur von **2a** (ohne Phenylringe und ohne Darstellung der Fehlordnung der Toluol-Moleküle).

dessen Bindungswinkel N–Cs–N von 93,3° und Cs–N–Cs von 86,7° nur wenig von der idealen Würfelstruktur abweichen (Abbildung 3). Die Toluol-Moleküle wirken als η^6-gebundene Brücken zwischen den Caesium-Atomen benachbarter Heterokubane, woraus eine dreidimensionale supramolekulare Struktur resultiert, deren Verknüpfungsprinzip in Abbildung 4 wiedergegeben ist. Die Bindungsbeziehung Cs···Toluol ist mit Cs···C-Abständen von 355,8 bis 357,7 pm nahezu symmetrisch, wobei einschränkend auf die

Tabelle 4 Ausgewählte Bindungslängen/pm und -winkel/° in $[CsNPPh_3]_4 \cdot 2$ Toluol $\cdot 3^3/_4$ Hexan (**2a**)

Cs(1)-N(1)	299.3(5)	N(1)-P(1)	153.6(9)
		C(1)-P(1)	184.2(9)
Cs(1)···C(7, 7F, 7G)	357.7(7)	Cs(1)···C(7C, 7D, 7E)	355.8(7)
N(1)-Cs(1)-N(1A)	93.3(2)	Cs(1)-N(1)-P(1)	127.6(1)
Cs(1)-N(1)-Cs(1A)	86.7(2)	N(1)-P(1)-C(1)	116.6(4)

Fehlordnung der Toluol-Moleküle hingewiesen sei. Die auf diese Weise sehr locker gepackte Struktur wird durch die eingelagerten, ebenfalls fehlgeordneten Hexan-Moleküle aufgefüllt, so daß sich die $[CsNPPh_3]_4$-Moleküle gleichsam in einer Lösungsmittel-Matrix befinden, die ihnen selbst bei –150 °C noch eine relativ große thermische Beweglichkeit gestattet. Man erkennt dies an den relativ hohen Temperaturfaktoren der Atomlagen.

Heterokuban-Strukturen des Caesiums wie in **2a** und **2b** (s.u.) wurden erst kürzlich anhand der mit $[CsNPPh_3]_4$ valenzisoelektronischen Verbindungen Caesium-t-butanolat $[CsO^tBu]_4$ [22] und Caesium(trimethylsilyl)amid $[Cs(HNSiMe_3)]_4$ [23] beschrieben. Im Vergleich mit letzterer Verbindung, deren Cs–N-Abstände 291,5 pm betragen [23], sind die Cs–N-Abstände in **2a** mit 299,3 pm deutlich länger, was vor allem mit den stark ionischen Bindungen Cs···N zusammenhängt, die sich auch im ^{31}P-NMR-Spektrum widerspiegelt (s.o.). Hierzu passen auch die sehr kurzen PN-Abstände in **2a**, die mit 153,6 pm ähnlich kurz sind wie in **1** und am unteren Ende des als Doppelbindungsbereich von 154–165 pm angesehenen Abstandes angetroffen werden.

Die im Vergleich mit $[Cs(HNSiMe_3)]_4$ [23] längeren Cs–N-Abstände in **2a** sind allerdings auch durch die zusätzliche Koordination mit den verbrückenden Toluol-Molekülen bedingt. Etwas länger sind die Cs–N-Abstände in $[CsN(SiMe_3)_2]_2 \cdot$ Toluol [24] mit 307,2 pm, in dem die Toluol-Moleküle wie in **2a** Brükkenfunktion zwischen den Caesium-Ionen haben, so daß eine eindimensionale supramolekulare Struktur resultiert. Bedingt durch den großen Raumanspruch der Bis(trimethylsilyl)amido-Gruppen sind die Cs–N-Abstände trotz kleinerer Koordinationszahl an den Caesium-Ionen etwas länger als in **2a**. Dagegen sind die Cs···C-Kontakte ähnlich lang wie in **2a**; sie entsprechen damit auch Erfahrungswerten in anderen Caesium-Aromaten-Komplexen [21], wie beispielsweise in dem Caesium-Benzylgallat $[Cs(Toluol)_{0.5}(C_6H_5CH_2)_3GaN_3]$ [25] mit Cs···C-Kontakten von 354,9 pm.

*3.3 $[CsNPPh_3]_4 \cdot 2$ Toluol (**2b**)*

Auch **2b** realisiert als Strukturmotiv das Cs_4N_4-Heterokuban-Gerüst, allerdings mit deutlichen Abweichungen von der idealen Würfelstruktur (Abbil-

dung 5). Dies bezieht sich sowohl auf die unterschiedlich langen Cs–N-Kontakte, die im Gegensatz zu dem hochsymmetrischen 2a nun zwischen 292,3 und 337,7 pm variieren, als auch auf die Bindungswinkel NCsN (83,1–96,9°) und CsNCs (81,8–96,4°). Die wesentlichen Ursachen hierfür sind die außerordentlich komplexen intra- und intermolekularen Wechselwirkungen der für alle vier Caesium-Ionen unterschiedlichen Interaktionen mit den Phenylresten der ($NPPh_3^-$)-Gruppen und mit den eingelagerten Toluol-Molekülen. Von diesen hat nun nur noch eines Brükkenfunktion zu benachbarten Heterokubanen, während das andere (an Cs (4)) terminal koordiniert ist.

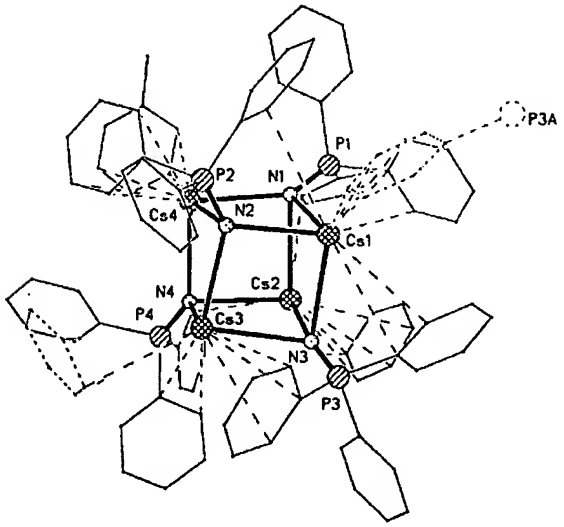

Abb. 5 Molekülstruktur von $[CsNPPh_3]_4 \cdot 2\,Toluol$ (2b) mit der Darstellung der intra- und intermolekularen Interaktion von Phenylringen und Toluol-Molekülen mit den Caesium-Atomen.

Die Folge davon ist die Ausbildung einer eindimensionalen, supramolekularen Aggregation, in der die Heterokuban-Moleküle eine Zickzack-Kette bilden (Abbildung 6).

Im einzelnen bilden die Caesium-Ionen in **2b** die folgenden Koordinationsmotive: Cs(1) wird von zwei Phenylringen intramolekular mit Abständen Cs(1)···C(37, 38) von 355,6 bis 384,0 pm und von einem Phenylring einer benachbarten ($NPPh_3^-$)-Gruppe mit Abständen Cs(1)···C(40 A, 41 A) von 361,5 bis 371,9 pm koordiniert.

Cs(2) bildet zwei intramolekulare Phenyl-Kontakte aus, nämlich Cs(2)···C(2) mit 388,7 pm und Cs(2)···C(56) mit 391,4 pm. Zusätzlich ist es von einem Toluol-Molekül mit Brückenfunktion (zwischen C(2) und C(3)) mit Abständen Cs(2)···C(101 bis 104) von 362,6 bis 388,9 pm koordiniert.

Ähnlich sind die von Cs(3) ausgehenden Kontakte zu dem Toluol-Molekül mit Brückenfunktion (zwischen C(3) und C(2)) mit Abständen Cs(3)···C(105 B und 106 B) von 388,4 pm. Darüberhinaus ist Cs(3) noch von zwei C-Atomen einer intramolekularen Phenylgruppe mit Abständen Cs(3)···C(61, 62) von 353,3 und 383,0 pm koordiniert.

Cs(4) schließlich wird von vier C-Atomen eines terminal angeordneten Toluol-Moleküls mit Abständen Cs(4)···C(203 bis 206) von 369,1 bis 383,3 pm koordiniert, zusätzlich aber auch noch intramolekular von den C-Atomen eines Phenylringes mit Abständen Cs(4)···C(19 bis 24) von 348,9 bis 383,7 pm.

Alle beobachteten Caesium-Aromaten-Kontakte bewegen sich damit im Erwartungsbereich [21]. Als Beispiele seien genannt $[Cs\{C(SiMe_3)_3\}(C_6H_6)_3]$ [26] mit Abständen von 343,3–379,0 pm und $[Cs(C_7H_8)_{0.5}(C_6H_5CH_2)_3GaN_3]$ [25] mit Abständen von 357,7 bis 379,7 pm.

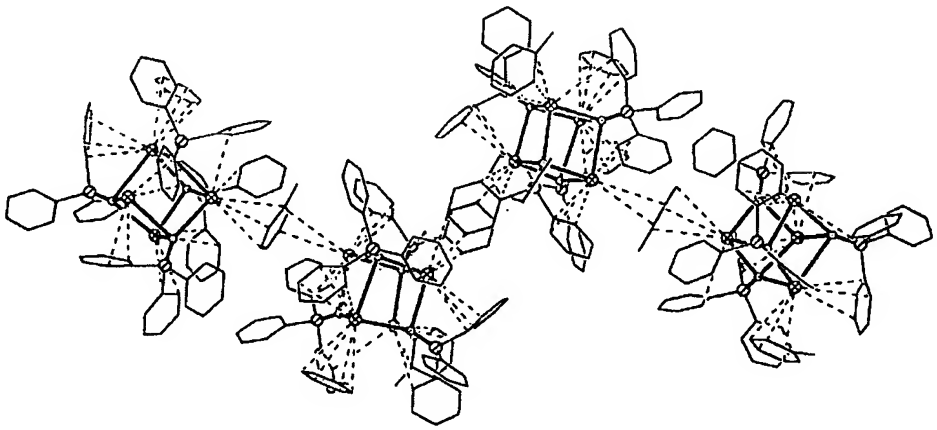

Abb. 6 Ausschnitt aus der durch Phenylreste und Toluol-Moleküle vermittelten eindimensionalen supramolekularen Zickzack-Kette in der Struktur von **2b**.

Tabelle 5 Ausgewählte Bindungslängen/pm und -winkel/° in $[CsNPPh_3]_4 \cdot 2$Toluol (2b)

Cs(1)-N(1)	304.0(3)	Cs(3)-N(2)	296.4(3)
Cs(1)-N(2)	293.0(3)	Cs(3)-N(3)	315.2(3)
Cs(1)-N(3)	306.0(3)	Cs(3)-N(4)	306.8(3)
Cs(1)···C(7)	356.6(3)	Cs(3)···C(43)	353.5(4)
Cs(1)···C(8)	380.8(4)	Cs(3)···C(44)	359.8(5)
Cs(1)···C(12)	371.7(4)	Cs(3)···C(48)	380.8(5)
Cs(1)···C(32)	378.0(4)	Cs(3)···C(61)	383.0(3)
Cs(1)···C(37)	384.0(4)	Cs(3)···C(62)	353.3(4)
Cs(1)···C(38)	355.6(4)	Cs(3)···C(105 B)	388.8(6)
Cs(1)···C(40 A)	371.9(5)	Cs(3)···C(106 B)	388.1(7)
Cs(1)···C(41 A)	361.5(4)	Cs(4)-N(1)	292.3(3)
Cs(2)-N(1)	311.9(3)	Cs(4)-N(2)	337.7(3)
Cs(2)-N(3)	299.4(3)	Cs(4)-N(4)	293.2(3)
Cs(2)-N(4)	300.7(3)	Cs(4)···C(19)	348.9(3)
Cs(2)···C(2)	388.7(5)	Cs(4)···C(20)	376.0(4)
Cs(2)···C(101)	386.5(6)	Cs(4)···C(23)	383.7(4)
Cs(2)···C(102)	362.6(5)	Cs(4)···C(24)	354.2(4)
Cs(2)···C(103)	366.1(6)	Cs(4)···C(203)	382.2(8)
Cs(2)···C(104)	388.9(7)	Cs(4)···C(204)	369.1(7)
Cs(2)···C(56)	391.4(7)	Cs(4)···C(205)	369.2(8)
		Cs(4)···C(206)	383.3(7)
N(1)-P(1)	153.1(3)	N(3)-P(3)	152.6(3)
N(2)-P(2)	153.2(3)	N(4)-P(4)	153.0(3)
N(1)-Cs(1)-N(2)	89.20(9)	Cs(1)-N(1)-Cs(2)	81.75(8)
N(1)-Cs(1)-N(3)	96.88(8)	Cs(1)-N(1)-Cs(4)	96.44(9)
N(2)-Cs(1)-N(3)	91.43(8)	Cs(2)-N(1)-Cs(4)	89.50(8)
N(1)-Cs(2)-N(3)	96.60(8)	Cs(1)-N(2)-Cs(3)	92.63(8)
N(1)-Cs(2)-N(4)	86.89(8)	Cs(1)-N(2)-Cs(4)	89.41(8)
N(3)-Cs(2)-N(4)	86.83(9)	Cs(3)-N(2)-Cs(4)	82.80(8)
N(2)-Cs(3)-N(3)	89.01(8)	Cs(1)-N(3)-Cs(2)	83.47(7)
N(2)-Cs(3)-N(4)	95.94(9)	Cs(1)-N(3)-Cs(3)	86.63(8)
N(3)-Cs(3)-N(4)	83.06(8)	Cs(2)-N(3)-Cs(3)	93.63(9)
N(1)-Cs(4)-N(2)	83.12(8)	Cs(2)-N(4)-Cs(3)	95.10(9)
N(1)-Cs(4)-N(4)	92.05(9)	Cs(2)-N(4)-Cs(4)	91.52(8)
N(2)-Cs(4)-N(4)	90.24(8)	Cs(3)-N(4)-Cs(4)	88.94(8)
Cs(1)-N(1)-P(1)	109.9(2)	Cs(1)-N(3)-P(3)	110.5(1)
Cs(2)-N(1)-P(1)	115.4(2)	Cs(2)-N(3)-P(3)	154.6(2)
Cs(4)-N(1)-P(1)	145.5(2)	Cs(3)-N(3)-P(3)	107.9(2)
Cs(1)-N(2)-P(2)	128.2(2)	Cs(2)-N(4)-P(4)	116.3(2)
Cs(3)-N(2)-P(2)	139.0(2)	Cs(3)-N(4)-P(4)	113.2(2)
Cs(4)-N(2)-P(2)	99.5(2)	Cs(4)-N(4)-P(4)	141.2(2)

Experimenteller Teil

Die Versuche erfordern Ausschluß von Feuchtigkeit und Sauerstoff. Alle Handlungen wurden unter Argon ausgeführt. THF, Toluol und Hexan wurden über K/Na-Legierung destilliert. Ph_3PI_2 [9] und Et_3PBr_2 [9] wurden nach Literaturvorschrift dargestellt. Ammoniak 3.8 (Messer-Griesheim), KH (Merck-Schuchardt, Hohenbrunn), Rb und Cs (Aldrich) waren handelsübliche Chemikalien. Die IR-Spektren wurden mit einem Bruker IFS-86-Gerät ausgeführt, CsI- und Polyethylenscheiben, Nujol-Verreibungen. Für NMR-Spektren stand ein Bruker-Gerät AM-400 zur Verfügung.

$[RbNPPh_3]_6 \cdot 4^1/_2$Toluol (1). Bei –78 °C wird auf 3.06 g Rb (35,8 mmol) in Gegenwart katalytischer Mengen $Fe(NO_3)_3 \cdot 9H_2O$ 40 mL NH_3 liq. kondensiert. Die blaue Lösung entfärbt sich innerhalb von 2,5 h unter Bildung einer klaren, leicht gelblichen Lösung von $RbNH_2$ in Ammoniak. Anschließend werden unter starkem Rühren 5.21 g Ph_3PI_2 (10,10 mmol) langsam zugegeben, wobei der gelbe Feststoff in einen voluminösen beigefarbenen übergeht. Es wird 6 h nachgerührt, Ammoniak abgedampft und i. Vak. von flüchtigen Anteilen befreit. Der feste Rückstand wird mit 60 mL Toluol bei 20 °C extrahiert und stark eingeengt. Aus der gelben Lösung werden innerhalb von 12 h rautenförmige klare gelbe Einkristalle erhalten. Ausbeute: 1,28 g (3,54 mmol, 35% d.Th.). Die Ausbeute kann durch Verwendung eines Toluol/THF-Gemischs (1:1) und Fällung mit Hexan auf ca. 65% gesteigert werden. Im Vakuum wird Toluol bereitwillig abgegeben.

$C_{139,5}H_{126}N_6P_6Rb_6$ (2585,22)

Elementaranalysen für $C_{108}H_{90}N_6P_6Rb_6$ (2170,59): C 56, 79 (ber. 59,76), H 4,26 (4,18). N 3,91 (3,87)%.

IR/cm^{-1}: 1301 w, 1273 w, 1186 vst, 1165 vst, 1090 st, 1063 m, 1026 m, 997 w, 854 vw, 747 st, 730 st, 697 vst, 619 vw, 530 vst, 511 st, 466 m, 454 w, 444 w, 382 vw, 290 m, 198 m, 111 w.

$[CsNPPh_3]_6$ (2a, 2b). Ansatzgröße: 3,75 g Cs (28,2 mmol), 4,46 g Ph_3PI_2 (8,64 mmol); Reaktionsdurchführung wie bei 1. Nach beendeter Reaktion wird in 25 mL Toluol aufgenommen und bei RT extrahiert.

$[CsNPPh_3]_4$ ist gut in Toluol löslich, weswegen das Filtrat weitestgehend eingeengt und zur Fällung mit 80 mL Hexan versetzt wird. Nach Filtration des gelben Produkt-Pulvers wird beim Trocknen i. Vak. Toluol nicht abgegeben.

Ausbeute: 2,24 g $[CsNPPh_3]_4 \cdot 2$Toluol (57% d.Th.).

Einkristalle von $[CsNPPh_3]_4 \cdot 2$Toluol $\cdot 3^3/_4$Hexan (2a) wurden aus einer bei RT gesättigten Lösung von $CsNPPh_3$ in Toluol/Hexan (1:1) unter Krypton bzw. Xenon bei (25 °C als gelbe klare Oktaeder erhalten. Diese zerfallen außerhalb dieses Milieus zügig durch Abgabe von Hexan und Verlust des kristallinen Habitus zu $[CsNPPh_3]_4 \cdot 2$Toluol. Aus mit Hexan gefällten Lösungen unter Argon fällt 2a innerhalb von zwei Wochen ebenfalls aus. Einkristallines Material von $[CsNPPh_3]_4 \cdot 2$Toluol (2b) wird durch Zugabe von Toluol zu einer gesättigten Lösung von $CsNPPh_3$ in Toluol mit Hexan bei RT unter Argon in Form monokliner klarer gelber Stäbchen innerhalb von 12 h erhalten. Diese behalten beim Evakuieren im Vakuum ihren kristallinen Habitus, geben kein Toluol ab.

Elementaranalysen für $[CsNPPh_3]_4 \cdot 2$Toluol: $C_{86}H_{76}Cs_4N_4P_4$ (1821,09): C 53,88 (ber. 56,72), H 3,94 (4,21), N 3,07 (3,08), Cs 29,02 (29,19)%.

$[CsNPPh_3]_4 \cdot 2$Toluol $\cdot 3^3/_4$Hexan (2a)

IR/cm^{-1}: 1296 w, 1269 m, 1222 vw, 1183 vst, 1091 vst, 1061 m, 1028 m, 1013 vw, 996 w, 845 w, 747 vst, 728 st, 694 vst, 619 vw, 525 st, 505 m, 470 m, 464 m, 446 m, 289 m, 246 w, 195 m.

$[CsNPPh_3]_4 \cdot 2$Toluol (2b)

IR/cm^{-1}: 1300 w, 1272 w, 1220 vw, 1176 vst, 1092 vst, 1061 m, 1026 m, 998 w, 849 vw, 749 st, 738 st, 728 st, 696 vst, 618 vw, 529 vst, 522 vst, 511 st, 466 m, 438 w, 293 m, 196 m.

$[KNPPh_3]_6 \cdot 4$Toluol. Bei –78 °C werden zu 80 mL NH_3 liq. 5,62 g KH (140,5 mmol) langsam zugefügt, wobei sich unter H_2-Entwicklung eine weiß-graue Suspension bildet. Anschließend werden 21,34 g Ph_3PI_2 (41,35 mmol) portionsweise unter Bildung einer gelb-grünlichen Suspension zugegeben. Es wird 3 h nachgerührt. Nach Abdampfen des Ammoniaks und Evakuieren flüchtiger Bestandteile wird zweimal mit je 80 mL Toluol heiß extrahierend filtriert. Nach Einengen des Filtrats auf ca. 40 mL kann der Ausfall des in der Kälte schwerlöslichen Produktes durch Fällung mit Hexan vervollständigt werden. Nach Filtration und Trocknung i. Vak., bei dem nicht koordiniertes Toluol abgegeben wird, werden 6,35 g gelbes pulveriges $KNPPh_3 \cdot 2$Toluol (18,61 mmol, 45% d.Th.) erhalten. Die Ausbeute kann durch

Verwendung eines Toluol/THF-Gemischs (1:1) auf ca. 65% gesteigert werden.

$C_{136}H_{122}K_6N_6P_6$ (2260.94)

Elementaranalysen für $C_{122}H_{106}K_6N_6P_6$ (2076.66): C 63.46 (ber. 70.53), H 4.78 (5.14), N 4.00 (4.04), K 9.98 (11.26)%.

IR/cm^{-1}: 1304 w, 1271 w, 1186 vst, 1169 vst, 1096 st, 1065 m, 1026 m, 999 m, 754 m, 747 m, 731 w, 698 vst, 675 w, 619 vw, 536 vst, 529 vst, 461 m, 446 m.

$[KNPEt_3]_n$. Ansatzgröße: 7.84 g Et_3PBr_2 (28.20 mmol), 3.80 g KH (95.0 mmol); Reaktionsführung wie bei $[KNPPh_3]_6 \cdot 4$ Toluol. Nach erfolgter Zugabe von Et_3PBr_2 wird 2 h nachgerührt; anschließend werden 50 mL Hexan bei –78 °C langsam zugetropft und 3 h gerührt. Nach dem Auftauen wird von Ungelöstem filtriert und das Filtrat zur Trockne eingeengt, woraus $KNPEt_3$ spektroskopisch sauber erhalten wird. Das Produkt ist in *allen* gängigen Lösungsmitteln sehr gut löslich, greift aber protonenaktive an. Ausbeute: 4.34 g (90% d.Th.) solvatfreies $KNPEt_3$.

Elementaranalysen: $C_6H_{15}KNP$ (171.26): C 40.58 (ber. 42.08), H 8.57 (8.83), N 8.20 (8.18), K 22.29 (22.83)%.

IR/cm^{-1}: 1257 st, 1164 vst (br), 1087 w, 1034 m, 1012 m, 757 st, 743 st, 691 m, 673 m, 634 m, 621 m, 590 w, 464 w, 438 m, 376 m, 307 m, 249 m, 143 w.

NMR/Toluol-d_8: ^{1}H: 1.00/0.97 (t, 3 H, $^3J_{CH}$ = 6.4 Hz, P-CH_2-CH_3); 1.16 (m, 2 H, $^3J_{CH}$ = 7.8 Hz, P-CH_2-CH_3).

$[NaNPPh_3]_6 \cdot$ Toluol. 14.34 g Ph_3PI_2 (27.79 mmol) werden mit 4.52 g $NaNH_2$ (115.9 mmol) in 100 mL Toluol/THF (100:1) suspendiert und unter gelegentlichem Evakuieren des entstehenden Ammoniaks gerührt. Nach 1 h ist das gelbe FS-Gemisch in ein beigefarbenes übergegangen. Nach drei Tagen wird von Ungelöstem abfiltriert, einmal mit 20 mL Toluol gewaschen und das Filtrat sehr stark eingeengt. Daraus wird das Produkt mit 70 mL Hexan gefällt. Nach Filtration und Trocknung erhält man das Produkt als beiges Pulver. I. Vak. werden eingelagerte Lösungsmittelmoleküle abgegeben. Ausbeute: 6.82 g (22.78 mmol, 82% d. Th.)

$C_{115}H_{98}N_6Na_6P_6$ (1887.86)

Elementaranalysen für $C_{108}H_{90}N_6Na_6P_6$ (1795.72): C 71.27 (ber. 72.24), H 4.85 (5.05), N 4.48 (4.68), Na 7.68 (7.68)%.

IR/cm^{-1}: 1303 w, 1271 w, 1186 vst, 1098 st, 1065 m, 1025 m, 997 m, 919 w, 743 st, 735 m, 698 vst, 618 vw, 534 vst, 527 st, 516 m, 467 m, 444 m.

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Literatur

[1] K. Dehnicke, F. Weller, *Coord. Chem. Rev.* **1997**, *158*, 103.

[2] K. Dehnicke, J. Strähle, *Polyhedron* **1989**, *8*, 707; K. Dehnicke, M. Krieger, W. Massa, *Coord. Chem. Rev.* **1999**, *182*, 19.

[3] K. Weber, K. Korn, M. Schulz, K. Korth, J. Sundermeyer, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1315.

[4] A. Dietrich, B. Neumüller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1321.

[5] H. Schmidbaur, G. Jonas, *Chem. Ber.* **1967**, *100*, 1120.

[6] S. Anfang, G. Seybert, K. Harms, G. Geiseler, W. Massa, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1187.

[7] S. Anfang, K. Harms, F. Weller, O. Borgmeier, H. Lueken, H. Schilder, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1998**, *624*, 159; S. Anfang, T. Gröb, K. Harms, G. Seybert, W. Massa, A. Greiner, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1853.

[8] T. Gröb, *Dissertation*, Univ. Marburg 1999.

[9] N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard, P. J. Kobryn, *J. Chem. Soc., Dalton Trans.* **1993**, 101.

[10] S. M. Godfrey, C. A. McAuliffe, I. Mushtaq, R. G. Pritchard, J. M. Sheffield, *J. Chem. Soc., Dalton Trans.* **1998**, 3815.

[11] M. B. Hursthouse, N. P. Walker, C. P. Warrens, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **1985**, 1043.

[12] D. Nußhär, *Diplomarbeit*, Univ. Marburg 1990.

[13] H. J. Christau, J. Kadoura, L. Chiche, E. Torreilles, *Bull. Soc. Chim. Fr.* **1989**, 515.

[14] S. Anfang, *Dissertation*, Univ. Marburg 1997.

[15] S. Chitsaz, B. Neumüller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1999**, *625*, 9.

[16] T. Miekisch, *Dissertation*, Univ. Marburg 1996.

[17] A. S. Batsanov, M. G. Davidson, J. A. K. Howard, S. Lamb, C. Lustig, R. D. Price, *J. Chem. Soc., Chem. Commun.* **1997**, 1211.

[18] L. G. Hoard, R. A. Jacobson, *J. Chem. Soc. A* **1966**, 1203; A. F. Cameron, N. S. Hair, D. G. Norris, *Acta Crystallogr.* **1974**, *30 B*, 221; G. W. Adamson, J. C. Bart, *J. Chem. Soc. A* **1970**, 1452; P. Rademacher, *Strukturen organischer Moleküle*, Bd. 2, Verlag Chemie, Weinheim 1987.

[19] D. J. Brauer, H. Bürger, G. R. Liewald, *J. Organomet. Chem.* **1986**, *308*, 119.

[20] N. P. Lorenzen, J. Kopf, F. Olbrich, U. Schümann, E. Weiss, *Angew. Chem.* **1990**, *102*, 1481; *Angew. Chem. Int. Ed.* **1990**, *29*, 1441.

[21] J. D. Smith, *Adv. Organomet. Chem.* **1998**, *43*, 267.

[22] S. Mann, M. Jansen, *Z. Kristallogr.* **1994**, *209*, 852.

[23] K. F. Tesh, B. D. Jones, T. P. Hanusa, J. C. Huffman, *J. Am. Chem. Soc.* **1992**, *114*, 6590.

[24] S. Neander, U. Behrens, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1429.

[25] M. R. Kopp, B. Neumüller, *Organometallics* **1997**, *16*, 5623.

[26] C. Eaborn, K. Izod, J. D. Smith, *J. Organomet. Chem.* **1995**, *500*, 89.

[27] G. M. Sheldrick, *SHELXS-97*, Programm zur Lösung von Kristallstrukturen, Göttingen 1997; SHELXL-97, Programm zur Verfeinerung von Kristallstrukturen, Göttingen 1997.

[28] G. M. Sheldrick, *SHELXTL*, Release 5.03 for Siemens R3 Crystallographic Research Systems, Siemens Analytical X-Ray Instruments, Inc., Madison (WI), USA 1995.

Exhibit 3

Clayden et al., Organic Chemistry, Clayden, Greeves, Warren and Wothers, Oxford University Press 2001

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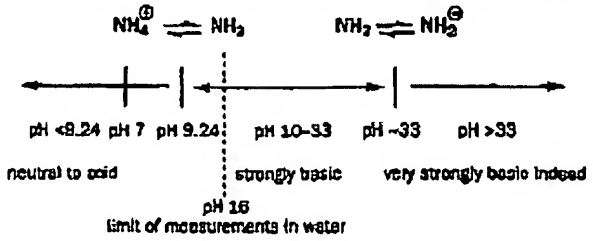
▶ **Get a feel for pK_as!** Remember that the pK_b also represents the pH when we have equal concentrations of acid and conjugate base; that is, NH_3 and NH_4^+. In this case: You know that ammonia is a weak base and that an aqueous solution is alkaline so it should come as no surprise that its pK_b is on the basic side of 7. To be exact, at pH 9.24 an aqueous solution of ammonia contains equal concentrations of ammonium ions and ammonia.

If we want to know the *basicity* of ammonia, we must look up the pK_a of its conjugat ammonium cation, NH_4^+, protonated ammonia. Its pK_a is 9.24 which means that am weaker base than hydroxide—the pK_a for water (the conjugate acid of hydroxide) is 15.7 Now we can summarize the states of ammonia at different pH values.



Scales for basicity—pK_B and pK_{BH}

The material in this box is quite mathematical and may be skipped if you find it too often.

It is often convenient to be able to refer to the basicity of a substance directly. In some texts a different scale is used, pK_B. This is derived from considering how much hydroxide ion a base forms in water rather than how much hydronium ion the conjugate acid forms.

For the pK_B scale:

$$B(aq) + H_2O \rightleftharpoons OH^-(aq) + BH^+(aq)$$

$$K_B = \frac{[OH^-][BH^+]}{[B]}$$

Hence

$$pK_B = -\log(K_B)$$

For the pK_A scale:

$$BH^+(aq) + H_2O \rightleftharpoons H_3O^+(aq) + B(aq)$$

$$K_A = \frac{[H_3O^+][B]}{[BH^+]}$$

Hence

$$pK_A = -\log(K_A)$$

Just as in the acid pK_a scale, the lower the pK_B t stronger the acid, in the basic pK_B scale, the lo pK_B, the stronger the base. The two scales are the product of the equilibrium constants simply ionic product of water.

$$K_B \times K_A = \frac{[OH^-][BH^+]}{[B]} \times \frac{[H_3O^+][B]}{[BH^+]}$$

$$= [OH^-][H_3O^+] = K_W = 10^{-14}$$

that is,

$$pK_A + pK_B = pK_W = 14$$

There is a separate scale for bases, but it seems have two different scales, the basic pK_B and the pK_{BH}, when one will do and so we will stick to pK_B. However, to avoid any misunderstandings that c from amphoteric compounds like ammonia, who around 33, we will either say:

- The pK_B of ammonia's conjugate acid is 9.24

or, more concisely,

- The pK_{BH} of ammonia is 9.24 (where pK_{BH} sim means the pK_B of the conjugate acid)

What factors affect how basic a compound is?

This really is the same as the question we were asking about the strength of an acid—the n ble' the base, the weaker it is. The more accessible the electrons are, the stronger the Therefore a negatively charged base is more likely to pick up a proton than a neutral one pound in which the negative charge is delocalized is going to be less basic than one with a n centrated, localized charge, and so on. We have seen that carboxylic acids are stronger a simple alcohols because the negative charge formed once we have lost a proton is delocali two oxygens in the carboxylate but localized on just one oxygen for the alkoxide. In other w alkoxide is a stronger base because its electrons are more available to be protonated. Since already considered anionic bases, we will now look in more detail at neutral bases.

▶ The most important factor in the strength of a base is which element the lone pair (or negative charge) is on. The more electronegative the element, the better it keeps hold of its electrons, and so the less available they are to accept a proton, and the weaker is the base.

There are two main factors that determine the strength of a neutral base: how accessil lone pair and to what extent can the resultant positive charge formed be stabilized either by ization or by the solvent. The accessibility of the lone pair depends on its energy—it is us HOMO of the molecule and so, the higher its energy, the more reactive it is and hence the the base. The lone pair is lowered in energy if it is on a very electronegative element or if delocalized in some manner.

This explains why ammonia is 10^{10} times more basic than water: since oxygen is more electronegative than nitrogen, its lone pair is lower in energy. In other words, the oxygen atom in water wants to keep hold of its electrons more than the nitrogen in ammonia does and is therefore less likely to donate them to a proton. The pK_{aH} for ammonia (that is, the pK_a for ammonium ion) is 9.24 whilst the pK_{aH} for water (the pK_a for hydronium ion) is −1.74. Nitrogen bases are the strongest neutral bases commonly encountered by the organic chemist and so we will pay most attention to these in the discussion that follows.

▶ pK_{aH}
We use pK_{aH} to mean the pK_a of the conjugate acid.

Neutral nitrogen bases

Ammonia is the simplest nitrogen base and has a pK_{aH} of 9.24. Any substituent that increases the electron density on the nitrogen therefore raises the energy of the lone pair thus making it more available for protonation and increasing the basicity of the amine (larger pK_{aH}). Conversely, any substituent that withdraws electron density from the nitrogen makes it less basic (smaller pK_{aH}).

Effects that increase the electron density on nitrogen

We can increase the electron density on nitrogen either by attaching an electron-releasing group or by conjugating the nitrogen with an electron-donating group. The simplest example of an electron-releasing group is an alkyl group (p. 416). If we successively substitute each hydrogen in ammonia by an electron-releasing alkyl group, we should increase the amine's basicity. The pK_{aH} values for various mono-, di-, and trisubstituted amines are shown in Table 8.4.

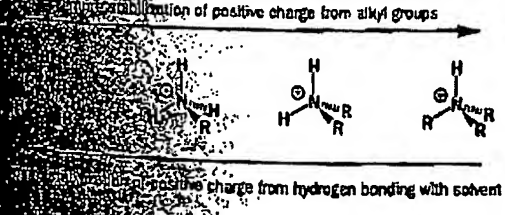
It is useful to notice in Table 8.4:

- All the amines have pK_{aH}s greater than that of ammonia (9.24)
- All the primary amines have approximately the same pK_{aH} (about 10.7)
- All the secondary amines have pK_{aH}s that are slightly higher
- All of the tertiary amines have pK_{aH}s lower than those of the primary amines

Table 8.4 pK_{aH} values for primary, secondary, and tertiary amines

R	pK_{aH} RNH_2	pK_{aH} R_2NH	pK_{aH} R_3N
Me	10.6	10.8	9.8
Et	10.7	11.0	10.8
*n*Pr	10.7	11.0	10.3
*n*Bu	10.7	11.3	9.9

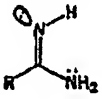
This last point indicates that our prediction that replacing the hydrogens by electron-releasing alkyl groups would increase basicity was correct. A strange feature though is that, whilst substituting one hydrogen of ammonia increases the basicity by more than a factor of ten (one pK_a unit), substituting two has little effect and in the trisubstituted amine the pK_{aH} is actually *lower*. So far we have only considered one factor of basicity, namely, the availability of the lone pair but the other factor, the stabilization of the resultant positive charge formed on protonation, is also important. Each successive alkyl group does stabilize the positive charge because it is electron-releasing but there is another stabilizing effect—every hydrogen attached directly to nitrogen will be hydrogen bonded with solvent water which helps to stabilize the charge: the more hydrogen bonding, the more stabilization. The basicity therefore results from a combination of effects: (1) the increased availability of the lone pair, (2) stabilization of the resultant positive charge, which increases with successive replacement of H atoms by alkyl groups; and (2) the stabilization due to solvation, an important part of which is hydrogen bonding and this effect decreases with increasing numbers of alkyl groups.



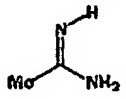
Gas phase acidity

If we look at the pK_{aH} values in the gas phase, we can eliminate the hydrogen bonding contribution and we find the basicity increases in the order we expect, that is, tertiary > secondary > primary.

Alkyl groups is the simplest way to increase the electron density on nitrogen but there is conjugation with an electron-donating group produces even stronger bases (p. 202) We can increase the electron density by using elements such as silicon. Silicon is more



an amidine

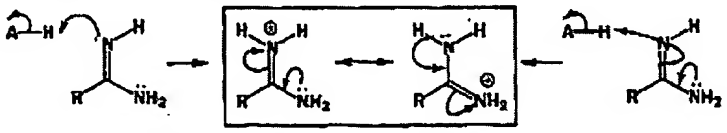


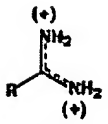
pK_{aH} 12.4

Amidines are stronger bases than amides or amines

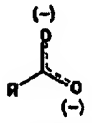
An amidine is the nitrogen equivalent of an amide—a C=NH group replaces the carbonyl. Amidines are much more basic than amides, the pK_{aH}s of amidines are larger than those of amides by about so there is an enormous factor of 10^{13} in favour of amidines. In fact, they are among the strongest neutral bases.

An amidine has two nitrogen atoms that could be protonated—one is sp^3 hybridized, the other sp^2 hybridized. We might expect the sp^3 nitrogen to be more basic but protonation occurs at the nitrogen atom. This happens because we have the same situation as with an amide: only if we protonate on the sp^2 nitrogen can the positive charge be delocalized over both nitrogens. We are using *both* lone pairs when we protonate on the sp^2 nitrogen.





amidinium cation



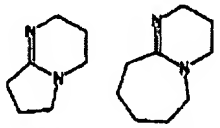
carboxylate anion

The electron density on the sp^2 nitrogen in an amidine is increased through conjugation with the sp^3 nitrogen. The delocalized amidinium cation has identical C–N bond lengths and a positive charge shared equally between the two nitrogen atoms. It is like a positively charged analogue of the carboxylate ion.

Amidine bases

Two frequently used amidine bases are DBN (1,5-diazabicyclo[3.4.0]nonene-5) and DBU (1,8-diazabicyclo[5.4.0]undecene-7).

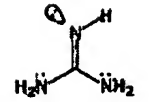
They are easier to make, more stable, and less volatile than simpler amidines.



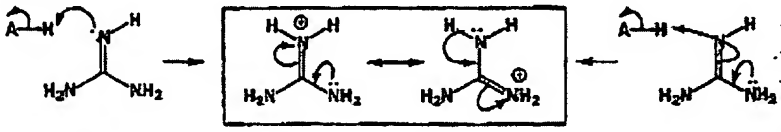
DBN DBU

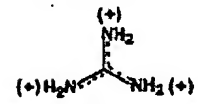
Guanidines are very strong bases

Even more basic is guanidine, pK_{aH} 13.6, nearly as strong a base as NaOH! On protonation, the positive charge can be delocalized over three nitrogen atoms to give a very stable cation. All three nitrogen lone pairs cooperate to donate electrons but protonation occurs, as before, on the sp^2 nitrogen atom.



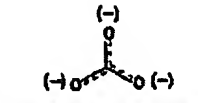
guanidine: pK_a 13.6





very stable guanidinium cation each (+) is a third of a positive charge

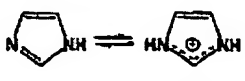
This time the resulting guanidinium ion can be compared to the very stable carbonate dianion. All three C–N bonds are the same length in the guanidinium ion and each nitrogen atom has the same charge (about one-third positive). In the carbonate dianion, all three C–O bonds are the same length and each oxygen atom has the same charge (about two-thirds negative as it is a dianion).



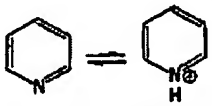
very stable carbonate dianion each (–) is two-thirds of a negative charge

Imidazoline is a simple cyclic amidine and its pK_{aH} value is just what we expect, around 11. Imidazole, on the other hand, is less basic (pK_{aH} 7.1) because both nitrogens are attached to an electron-withdrawing sp^2 carbon. However, imidazole, with its two nitrogen atoms, is much more basic than pyridine (pK_{aH} 5.2) because pyridine only has one nitrogen on which to stabilize the positive charge.

imidazoline pK_{aH} 11



imidazole pK_{aH} 7.1 imidazolium cation



pyridine pK_{aH} 5.2 pyridinium cation

X. RELATED PROCEEDINGS APPENDIX

None.